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121

QUARTERLY REPORT

NO. 1-3

PROJECT NO. E-102

PHYSICS OF SOLIDS

BY

E.J. SCHEIBNER, W.E. WOOLF,
VERNON CRAWFORD, JOSEPH WORTH, AND
R.B. BELSER

SEPTEMBER 30, 1953-MARCH 31, 1954

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of the Georgia Institute of Technology
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This report includes the work of
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I. ABSTRACT

Most of the work of this quarter was concerned with a study of methods for preparing surfaces of single metal crystals and polycrystalline metals. Electron diffraction patterns were obtained from polished and etched polycrystalline aluminum alloys and from aluminum single crystals.

A preliminary investigation was made of the methods for obtaining the orientation of single metal crystals. As a result of this investigation, it appears that the back-reflection Laue method is the simplest and most direct way of determining the orientation. When a single crystal surface is to be prepared parallel to a specific crystallographic plane, the angle between a prepared surface and the desired crystallographic plane can be measured precisely with the crystal orientation unit, but the back-reflection method is first used to determine the approximate orientation.

The interpretation of single-crystal electron diffraction patterns was undertaken with the object of determining the changes which occur in electron diffraction patterns when the crystal lattice departs from perfect periodicity.

Preliminary x-ray studies of dual-layer films have provided information on the advantages of each available technique. The back-reflection and diffractometer methods have relatively high resolution and are nondestructive. The powder method is preferable for identifying the phases present, but for determination of composition from lattice parameter measurements both of the other two methods are superior.

II. PURPOSE

The purpose of Project E-102, entitled "Physics of Solids," is to establish a research program in solid-state physics at the Experiment Station. The initial studies will provide information on techniques and methods of research, while later studies will be concerned with specific problems in the physics of solids. The initial stages will include:

1. Studies of the preparation of metal surfaces for examination by the reflection-electron diffraction method, optical microscopy utilizing the metallographic microscope, and electron microscopy of surface replicas. The preparation techniques to be studied should include mechanical grinding and polishing, etching, and electropolishing of small metal specimens.
2. Surface studies of polycrystalline metals to determine alloy constitution, the effect of etching, and the degree of distortion due to grinding and polishing.
3. Extension of surface studies to single metal crystals. The removal of the distorted surface layer to produce Kikuchi line electron diffraction patterns.

III. EXPERIMENTAL WORK

The experimental work of this quarter has been primarily that of developing techniques for preparing the surfaces of single crystal and polycrystalline metals. Space requirements in the diffraction chamber of the RCA-type EMU electron microscope limit the size of specimens that may be handled conveniently. Except for the handling of small-sized specimens, standard metallographic methods are used for preparation of surfaces, with care being taken to preserve the flatness of specimens and to limit, in so far as possible, the distortion of the surface layers introduced during mechanical polishing.

A. Preparation of Specimens

1. Size of Specimens

For examination by reflection-electron diffraction methods, 1/8-inch lengths are cut from a 1/4-inch-diameter round rod. This size specimen is easily attached to a standard reflection specimen holder by melting a small amount of sealing wax on the holder. The only limitation on the size of specimens from which surface replicas are obtained is that large specimens are difficult to polish uniformly. For studies of plastic deformation where it will be necessary to use fairly large tensile-test specimens, it may prove more advantageous to electropolish sections of the flat surface rather than attempt to polish the entire specimen surface.

2. Polishing and Etching

Metallographic techniques for polishing and etching metals as outlined in Kehl[1] and in the ASM Metals Handbook[2] are being used. In order to obtain uniformly thick specimens and to prevent the rounding off of their edges, three or four small specimens are mounted in a groove on a 1-inch-square brass

block with sealing wax or with a beeswax and rosin mixture. The groove (0.075 inch deep) in one surface of the block aids in obtaining approximately the same thickness for all small specimens.

In general, the mechanical polishing sequence is: (a) drawing the specimens slowly over a long-angle lathe file; (b) rough polishing on a series of emery papers of increasing fineness, Nos. 1-0-00-000; (c) polishing with 400-grit carborundum on a canvas duck-covered polishing wheel; (d) polishing with 600-grit carborundum on canvas duck; (e) fine polishing with No. 1 alumina on billiard cloth; (f) final polishing with magnesium oxide on a polishing cloth such as Selvyt, Kitten's Ear, or Miracloth. It has been found that for ordinary metallographic examination, step (f) is not always necessary. In steps (a) to (d) it is common practice to rotate the specimen 90 degrees between grinding stages and to continue grinding at one stage until all scratches from the preceding stage have been removed.

There is a tendency to form a distorted layer at the surface of a metal during mechanical polishing. Although this layer can usually be removed by alternately polishing and etching several times, the work is time consuming and the desired results are not always obtained, particularly when a soft metal is being polished. We have prepared a few specimens by electropolishing after grinding on the emery papers. This procedure avoids any unnecessary distortion and thus would appear to be well-suited for polishing the small specimens encountered in our work.

Since the optimum etch for examination of surfaces by electron diffraction and surface replica methods may not be the same as that for optical examination, considerable effort has been directed toward the determination of the proper

conditions for etching. Some success has been achieved with polycrystalline aluminum alloys as evidenced by the electron diffraction patterns of Figure 1. Both specimens were lightly etched* after electropolishing and rinsed through the sequence 1:1 methanol-HCl ⟶ 1:1 methanol-acetone ⟶ benzene ⟶ air dry, as suggested by Heidenreich.[3] The diffraction patterns are the normal face-centered cubic patterns for aluminum; the spotty appearance of the lines in the pattern of the high-purity aluminum alloy is indicative of a large grain size in the metal.

3. Single Crystals

Single crystals of aluminum, copper, and nickel have been obtained and are being prepared according to the following procedure: (a) grinding on a series of emery papers, Nos. 1-0-00-000-0000, lubricated with a paraffin in kerosene mixture (25 g paraffin per 500 ml kerosene); (b) electrolytic polishing; (c) etching.

The nature of the surface of single crystals is indicated by the type of reflection-electron diffraction pattern obtained. During the preparation of aluminum single crystals it was noted that when the electropolishing and etching are not sufficient, a diffraction pattern such as that of Figure 1A is obtained. This indicates that the distorted surface layer has not been removed completely and also that the portion of the layer remaining consists of finely divided crystallites randomly dispersed. After repolishing and etching, the electron diffraction pattern obtained is a pattern of Laue spots. The best condition of the surface of single crystals is that which gives a Kikuchi line

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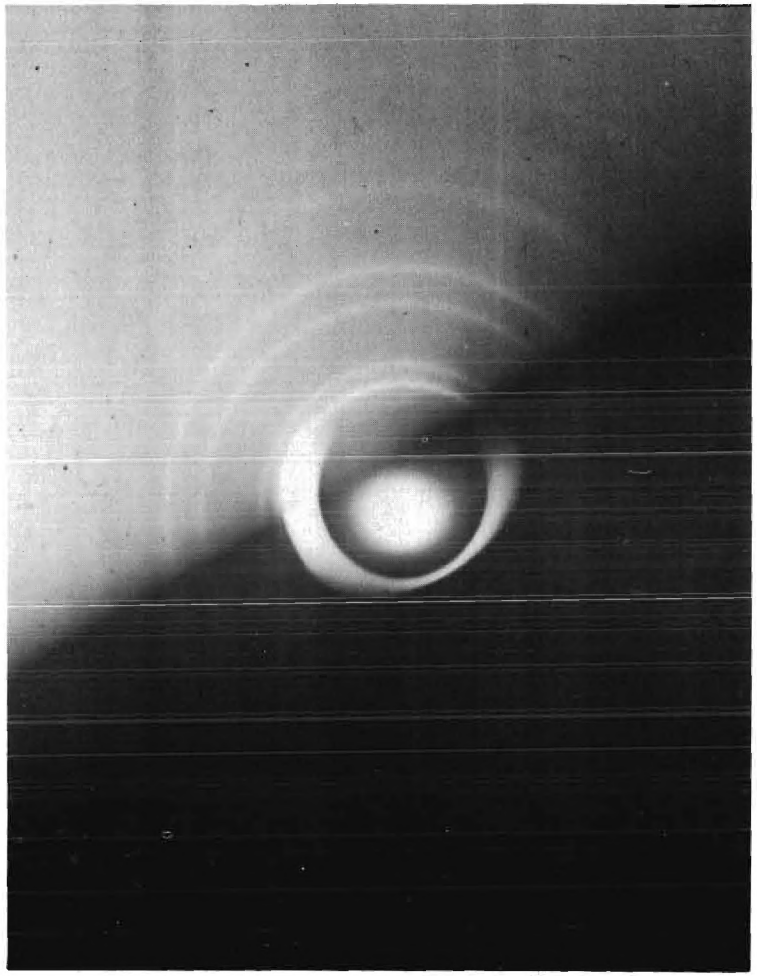
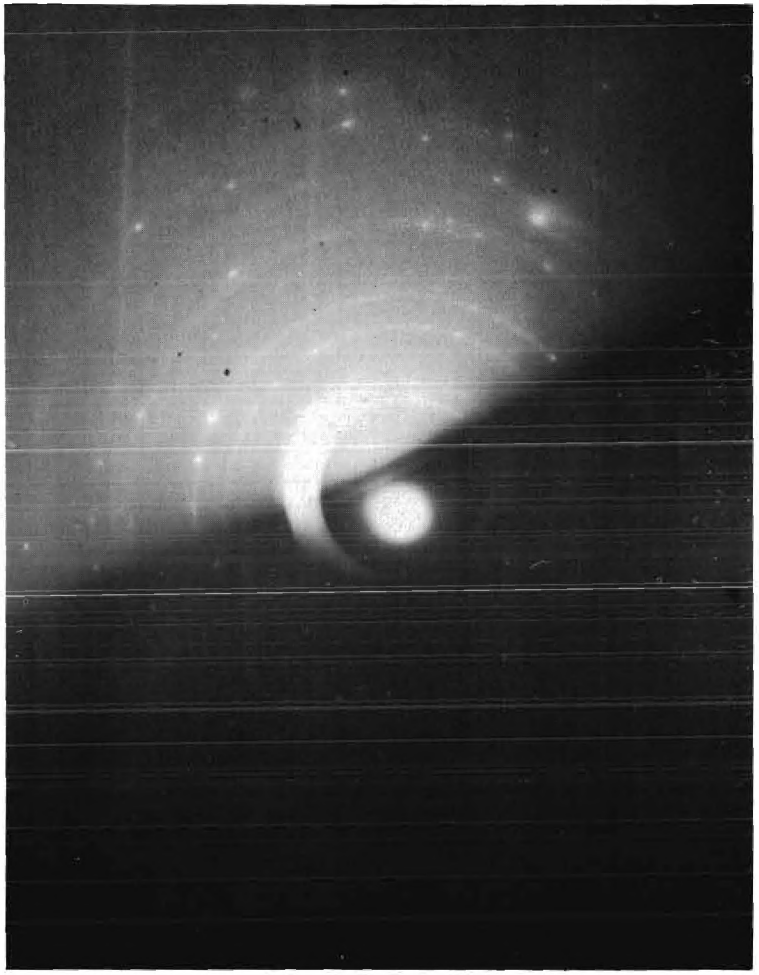
*The etchant has the composition: 20 cc conc. HCl; 5 cc conc. HNO_3; 5 cc conc. HF; 15 cc H_2O.



A. Reflection Pattern of Low-Grade Al Alloy; Small Grain Size.



B. Reflection Pattern of High-Purity Al Alloy; Large Grain Size.

Figure 1. Electron Diffraction Patterns of Polycrystalline Aluminum Specimens.

electron diffraction pattern.[4,5] The Kikuchi line pattern can only be obtained from single crystals when the degree of perfection of the crystal lattice extends over a wide area of the surface. Figure 2 is a typical pattern, the pairs of dark and light lines being Kikuchi lines. The phenomenon can be simply explained in terms of two scattering processes in separate parts of the crystal. Let us consider the pair of dark and light lines, P_1 and P_2, respectively. Electrons which would normally have gone to P_1 undergo Bragg reflections by a set of atomic planes and appear instead at P_2. Those electrons which would have gone to P_2 are reflected by the same set of planes to P_1. Since the intensity distribution of scattered electrons falls off rapidly with angle or distance from the central spot, the net effect is to cause a deficiency or dark line at P_1 and an excess or light line at P_2.

B. X-Ray Orientation of Single Crystals

Several physical properties of materials show anisotropy, that is, the property varies with crystallographic direction. It is important, therefore, to determine the orientation of single crystals and to be able to prepare surfaces of single crystals parallel to any desired crystallographic plane.

Optical methods for orienting single metal crystals have been used by Gwathmey[6] and others, but, in general, more exact orientation is obtained by an x-ray method.[7] This method consists of taking a back-reflection x-ray diffraction pattern from a surface of the crystal and comparing the stereographic projection obtained from that pattern with a standard stereographic projection of a crystal of the same structure. For the details of the back-reflection method one may refer to Barrett[8] or to the tentative standards on x-ray orientation of single crystals included in the ASTM Standards.[9]

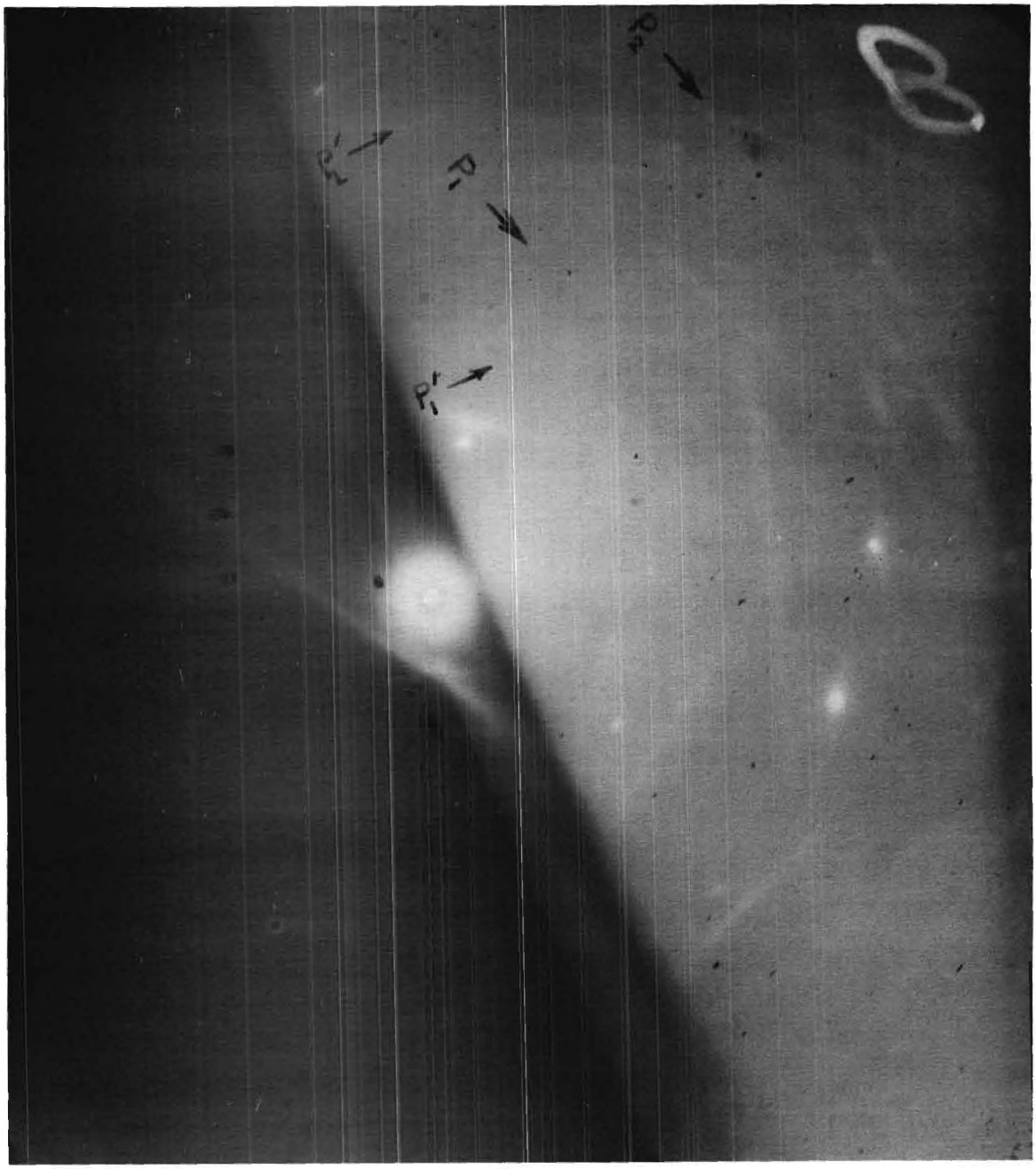


Figure 2. A Kikuchi Line Electron Diffraction Pattern.

C. Examination of Surfaces

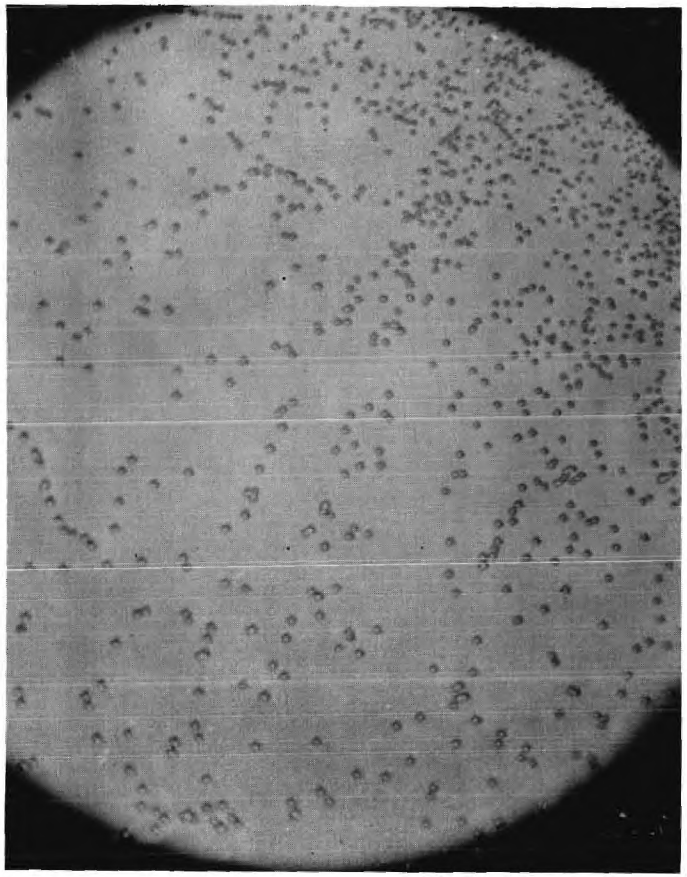
This section is intended to summarize the methods available for the study of surface conditions of solids and for electron microscopy to illustrate the formation of slip lines after plastic deformation.

1. Optical Microscopy

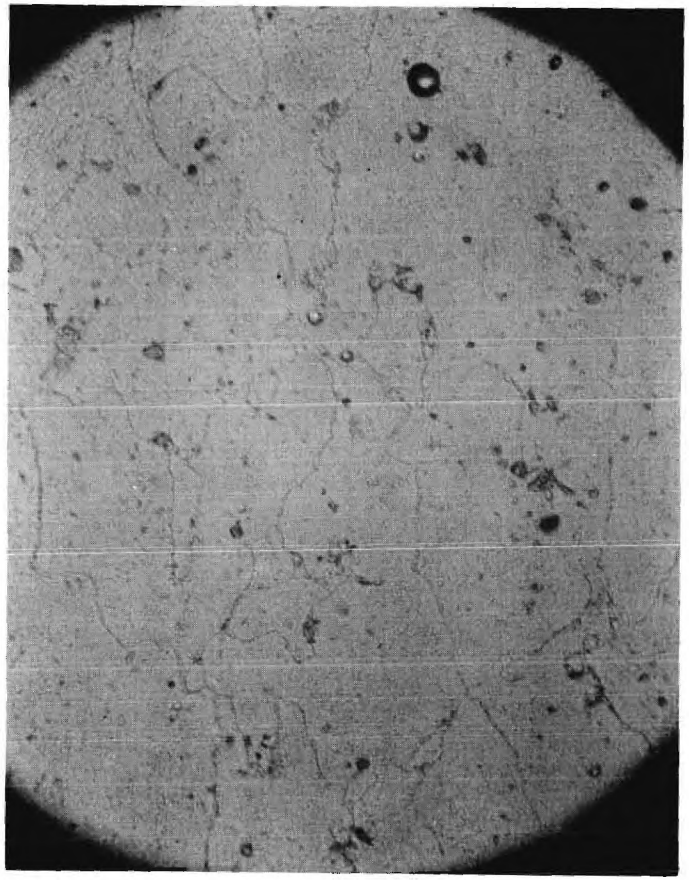
In general, optical examination of surfaces provides information on the macroscopic detail of the surface. Identification of constituents in polycrystalline metals can be accomplished by observing the effect of various etching reagents on the appearance of the surface. When etching has occurred on the surface of a single crystal, optical studies of the etch pits may help to determine the orientation of the crystal, particularly where it is known that the etching reagent used develops certain crystallographic planes. Figure 3A shows the surface of a single crystal of aluminum after electropolishing. Some slight etching is evident in the photograph. Figure 3B is an optical micrograph of the surface of a polycrystalline aluminum specimen after electropolishing and etching by sputtering.

2. Electron Microscopy

The study of surfaces of solid specimens by electron microscopy depends upon the ability to form a representative surface replica. The method of examination is well discussed in recent publications on electron microscopy.[10,11] The study of the plastic deformation of metals provides an excellent illustration of the usefulness of the electron microscope for solid-state problems which affect the surface structure. It is known that most metals undergo a process of slip along certain well-defined crystallographic planes when deformed by compression or tension. The intersection of the slip planes



A. Surface of Aluminum Single Crystal after Electropolishing.



B. Surface of Polycrystalline Aluminum after Electropolishing and Etching by Sputtering.

Figure 3. Optical Micrograph of Metal Surfaces.

with the surface of the specimen produces slip lines. Although the regions of slip or slip bands are visible with the light microscope, the finer slip lines can only be resolved in the electron microscope. The micrographs of Figure 4 from the paper by Kuhlmann-Wilsdorf and Wilsdorf[12] show the nature of slip and cross-slip on polycrystalline α-brass and on an aluminum crystal.

3. Electron Diffraction

The method of reflection-electron diffraction is discussed and illustrated in other sections of this report (sections III A and D). If one were to compare the special features which distinguish x-ray and electron diffraction, it would be evident that the outstanding difference between the two is the very small penetrating power of electrons. This low penetration results from the fact that the electrons are readily scattered by the atoms of the crystal lattice. At the glancing angles used in reflection diffraction work the penetration of the electron beam, normal to the surface, is of the order of 10 lattice planes, and, therefore, surface phenomena are best investigated by this method.

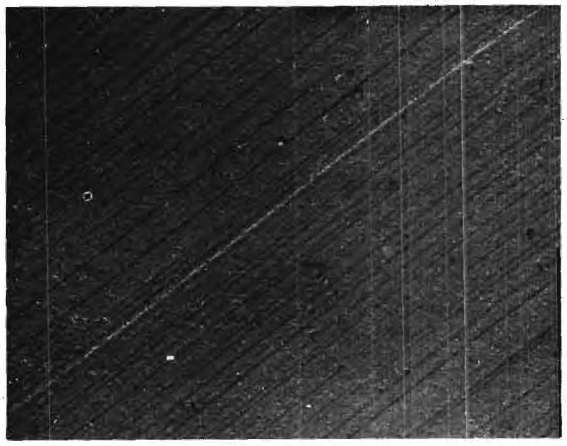
4. X-Ray Diffraction

The back-reflection Laue method, besides being useful for determining the orientation of single crystals, can also provide information on the nature of the surface layers. Although no such studies have been made so far, it should be possible to detect imperfections in the surface layers of single crystals by studying the departure from sharpness of the Laue spots.

D. Interpretation of Electron Diffraction Patterns

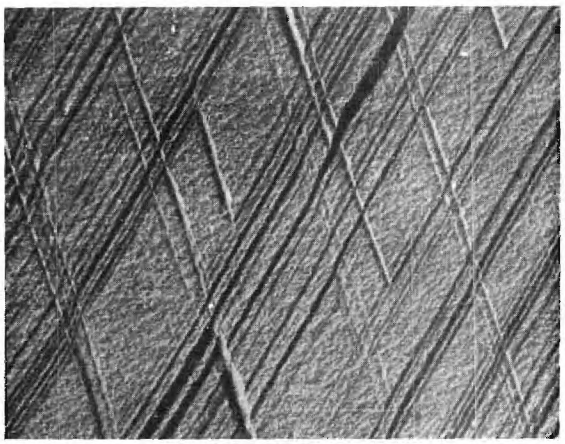
1. Polycrystalline Materials

The interpretation of electron diffraction patterns from polycrystalline materials is well summarized in a previous report by one of the authors



A. Closely Spaced Regular Slip Lines of Polycrystalline α-Brass; Elongation 5 Per Cent; 20,000x.

B. Two Systems of Slip Bands on Aluminum Crystal; Elongation 20 Per Cent; 7,500x.



C. Cross-Slip on Polycrystalline α-Brass; Elongation 15 Per Cent; 20,000x.

D. Peculiar Cross-Slip Near an Etch Pit in α-Brass; Elongation 5 Per Cent; 15,000x.

Figure 4. Electron Micrographs of Slip Lines Formed after Plastic Deformation.

under Project No. 163-105.[13] It may be worthwhile to emphasize, however, that single crystal specimens do not always give typical single crystal diffraction patterns. Because of the low penetration of electrons into the surface of reflection specimens the resulting pattern is extremely sensitive to changes in the surface layers. In particular, when a large distorted layer resulting from mechanical polishing is present on the surface of a single crystal, a pattern of rings will be obtained. The interpretation of the pattern would then give information on the crystal structure, the crystallite size in the distorted layer, and the presence of preferred orientation in the layer.

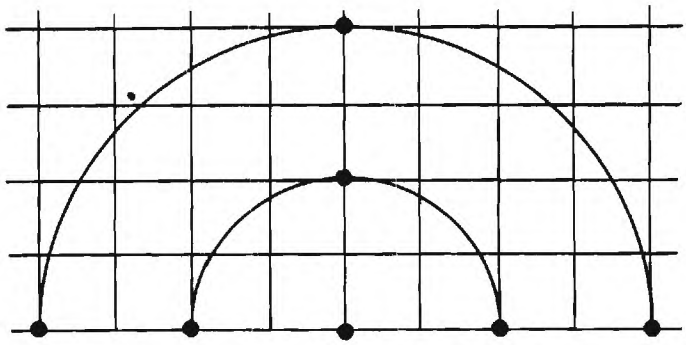
2. Single Crystals

The interpretation of electron diffraction patterns from single crystals as proposed by Kirchner and Raether[14] provides an explanation in terms of the conditions for constructive interference of electron waves corresponding to the three crystallographic axes of a crystal. A more detailed study is based on the concept of the reciprocal lattice. The reciprocal lattice method is an elegant way of interpreting electron diffraction patterns, as the resulting photograph represents in effect a plane through the reciprocal lattice with regions of high intensity corresponding to particular points of the lattice. Since this method is also basic to the analysis of x-ray precession-camera photographs, studies are being continued.

In order to illustrate Kirchner's method, let us assume that we have a cubic crystal with rows of atoms along each of the rectangular axes x, y, and z. Let us also assume that electrons are incident from the direction x on a perfect xy cleavage face. The conditions for constructive interference of the electron waves which arise from periodicity of the lattice in each of the three

directions, x, y, and z, may be stated separately. Let us suppose that the pattern is to be examined on a plane screen at a considerable distance from the crystal. Then corresponding to the periodicity in the z-direction (into the face of the crystal) constructive interference would be found along lines on the screen drawn parallel to the face of the crystal. Corresponding to the periodicity of the lattice parallel to the face of the crystal and at right angles to the beam (in the y-direction) conditions for constructive interference will be fulfilled along a series of hyperbolae on the screen, but under ordinary circumstances the curvature will be small, and as a simple approximation we may say that constructive interference will occur along a series of lines on the screen parallel to the z-axis (or the normal to the crystal surface). These two conditions for constructive interference taken together give the ordinary cross-grating pattern. There is, however, a third condition for constructive interference imposed by the periodicity of the crystal in the x-direction (or along the beam). The condition for constructive interference is approximately fulfilled over a small circular region centered at the intersection of the x-axis (or the axis of the original electron beam) with the screen. Surrounding this there is a region of destructive interference and outside of this again, a region of constructive interference.

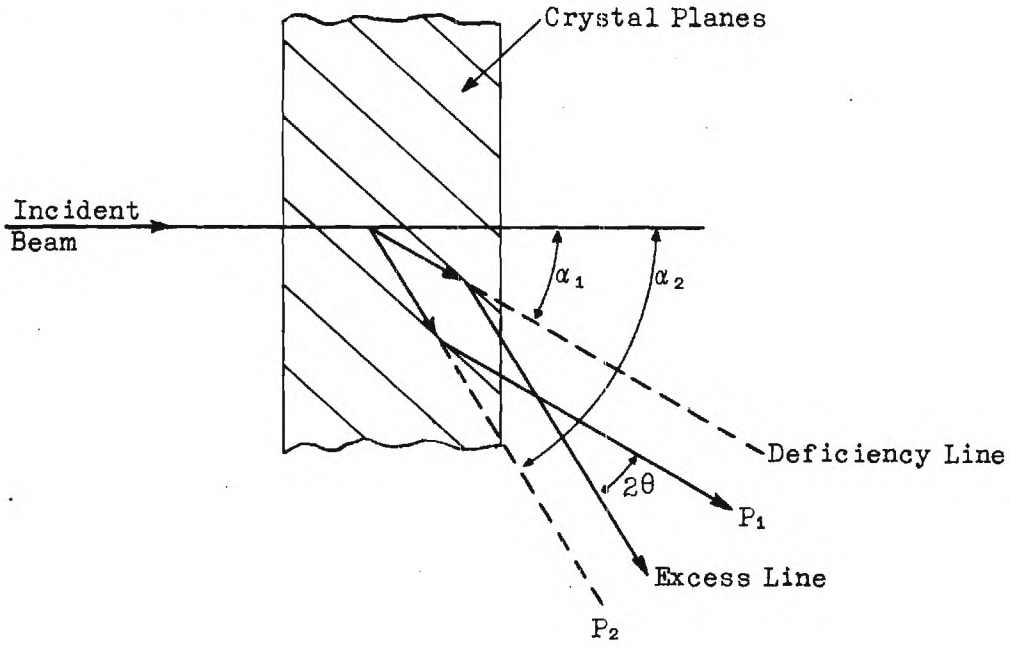
If on the screen we draw the curves of constructive interference, the figure would look something like that of the accompanying sketch. It is only where the intersection of crossed lines falls on one of the circles that the condition for maximum constructive interference is fulfilled, and if we were able to use effectively a very large perfect crystal, only these spots would appear in the pattern.



In practice there is some relaxation of all the interference conditions. It can be shown that the variation in the amplitude which is caused by scattering from atoms along the path of the electron beam is relatively slow, and for this reason the circles should be replaced by rather broad bands so that the diffraction would show a gradual transition from constructive interference to destructive interference and back to constructive interference. In the second place, the electrons do not penetrate the crystal deeply so that the interference condition along the horizontal lines shown in the figure is considerably relaxed. The most rigid interference condition is apt to be that corresponding to the vertical lines in the figure, but even this condition can be considerably relaxed if the periodicity of the crystal surface does not persist over large numbers of atoms in the y-direction. Thus, the relaxation of the interference conditions can be used to give a qualitative estimate of the degree of perfection of the crystal surface.

Where the perfection of the crystal lattice extends over a considerable area of the surface, one may obtain Kikuchi line patterns. As explained earlier in section III A3, the Kikuchi line pattern has as its main features pairs of black and white lines superimposed on a relatively high background in addition to the usual Laue or Bragg spots. The background is due to the

incoherent scattering of the incident beam as it traverses the crystal. The divergent beam of electrons in the crystal will be diffracted by a set of planes whenever those electrons incident upon the planes satisfy the Bragg condition. The situation is shown schematically in the following sketch where two rays of the divergent beam at angles α_1 and α_2 with the incident beam meet a set of planes at the Bragg angle θ.



As a result of the Bragg reflection, those electrons at angle α_1, that would normally have appeared at P_1, are diffracted to P_2; and those at angle α_2 are diffracted to P_1 instead of proceeding to P_2. But since the intensity in the divergent beam decreases with increasing angle of scattering and since $\alpha_2 > \alpha_1$, P_2 receives more electrons that should have gone to P_1 than P_1 receives by diffraction. P_1 thus exhibits a deficiency of electrons relative to the background and P_2 an excess. The lines observed are actually hyperbolae since they result from the intersection of a cone and a plane.

In order that the lines be visible on the photographic plate it is necessary that the net transfer of electrons from P_1 to P_2 be in excess of a minimum number, say N_o. Now N_o is determined by the volume of crystal which can diffract electrons to P_1 and P_2 or to the thickness of crystal in the direction of the incident beam for the case of a thin slab, that is, N_o is sensitive to the perfection of alignment of various portions of the crystal, for if small portions are disoriented, each portion will not diffract electrons accurately to P_1 and P_2 and the lines will be broad. The broader the line, the lower the contrast, and thus the lines usually disappear by the time the breadth exceeds about 10^{-3} rad. The presence of Kikuchi lines then may be taken to indicate that the periodicity persists over relatively long distances in the crystal.

E. X-Ray Studies of Dual-Layer Films

The techniques of Burr, Coleman, and Davey[15] have been used to study the alloying of films of two metals deposited successively on a glass microscope slide. After deposition the films were heated to increase diffusion of the metals.

Both the Geiger-counter diffractometer and the powder camera have been used. The dual films were placed on the diffractometer in the mount normally used for flat powder samples. The metal films were 2,000 to 3,000 Å thick and hence much less than the optimum thickness, causing the diffraction peaks to have a low intensity. These weak peaks were superimposed on a high background resulting from scattering by the glass. For this reason the results of this method were unsatisfactory in most cases.

The other technique consisted of scraping the metal from the microscope slide and sealing it in a capillary tube. This sample was then mounted in a

Hull-Debye-Scherrer powder camera in the usual way. In most cases the powder photographs contained enough diffraction lines to permit identification of the phases present.

Another available technique has thus far not been used. In the back-reflection camera, x-ray diffraction lines can be observed at angles near the limit determined by the wave length of the radiation used. For these lines, the interplanar spacing can be determined more accurately than at lower angles because the variation of sin θ is small. The method will be used principally in determining the lattice parameter of solid solutions of two metals. If the variation of lattice parameter with composition is known, the composition can then be determined.

Each method has some advantage. The diffractometer and back-reflection methods have relatively high resolution and are nondestructive. In the powder method, the ratio of the intensity in the diffraction maxima to the background is much higher. This method is preferable for identifying the phases present, but for determination of composition from lattice parameter measurements both of the other two methods are superior.

The x-ray studies of dual films have been most successful in systems in which the equilibrium diagram and the diffraction patterns of the various phases have been determined. If comparison x-ray data are available, the phases present and the approximate composition can be determined. In addition, incomplete diffusion can be detected in some cases by the presence of three distinct phases.

A preliminary survey has been made of the information available on the phase diagrams of the systems whose semiconducting properties will be studied

during the next quarter. The principal source of this information has been the Metals Handbook, 1948 Edition (American Society for Metals, Cleveland, Ohio, 1948).

The solubility of aluminum in antimony or antimony in aluminum is less than 0.1 per cent at room temperature. An intermetallic phase at 50 atomic per cent has been reported.

The solubilities of aluminum in bismuth and bismuth in aluminum have not been determined but are believed to be low. No intermediate phases have been reported.

The indium-antimony system has one intermediate phase, reported by Goldschmidt[16] and confirmed by Liu and Peretti[17] who established the complete diagram.

Peretti and Carapella[18] report two phases in the indium-bismuth system: one corresponding to In_2Bi and one to InBi. The structures have not been determined.

No information has been found on the aluminum-arsenic, indium-arsenic, gallium-arsenic, gallium-antimony or gallium-bismuth phase diagrams.

IV. PROGRAM FOR NEXT INTERVAL

1. Continuation of studies on the preparation of surfaces, with emphasis being placed on the proper treatment of single metal crystals in order to produce the optimum condition of the crystal surface. This condition will be indicated by a Kikuchi line electron diffraction pattern.

2. Modification of present x-ray facilities to provide complete orientation of single crystals by the back-reflection method and precise determination of angle between a prepared surface and a specific crystallographic plane.

3. Interpretation of electron and x-ray diffraction patterns of single crystals by means of the reciprocal lattice for nearly perfect crystals and a study of the changes occurring in reciprocal space when the crystals contain imperfections.

4. Continuation of studies on dual-layer films to provide information on the mechanism of diffusion in thin films through the determination of binary alloy formation.

5. Resistivity and Hall-effect measurements of thin films of alloys formed by diffusion in dual-layer films to determine the existance of semiconducting properties.

Approved:

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Project Director

Herschel H. Cudd, Director
Engineering Experiment Station

Respectfully submitted:

Edwin J. Scheibner
Assistant Project Director

William E. Woolf
Research Physicist

V. APPENDIX

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DECEMBER 31, 1953

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This Report Contains 14 Pages

LIST OF FIGURES

I. ABSTRACT

Most of the work this quarter was concerned with collecting and assembling the equipment needed for measurements of conductivities of thin metallic films. Some study has been made concerning the best method for measuring the thickness of the films. The problem of how to translate electrical conductivity and Hall coefficient data into information relating to the mobility and nature of the current carriers has been studied. A new crystal holder for a back-reflection X-ray camera has been designed, constructed, and given preliminary tests.

II. PURPOSE

The purpose of this project is to get research in the field of solid state physics started at the Engineering Experiment Station of the Georgia Institute of Technology. Various problems in this general field will be studied for the purposes of training some investigators in the field of solid state research, of making the best use of the existing facilities, and of acquiring such additional research equipment as is needed to maintain an active solid state program. The scope of the project will undoubtedly increase as work progresses. Specific problems to be studied include:

1. Studies of the preparation of metal surfaces for examination by electron diffraction, optical microscopy, and electron microscopy of surface replicas;

2. Surface studies of single crystals;

3. The properties of single and dual layer films.

III. EXPERIMENTAL AND THEORETICAL WORK

A. Thin Films

1. Experimental

The principal experimental work of this quarter consisted of construction and preliminary test of a circuit to be utilized in the measurement of electrical conductivity and Hall coefficient of thin metallic films. The circuit is essentially the same as one used by Pearson and Bardeen.[1] As a beginning only conductivities will be measured, and these only at room temperature.

A schematic diagram of the circuit, as first tried, appears in Figure 3.1. The micromanipulator contactor was modified to allow for a larger range of sample sizes, for measurement of potential at any point on the sample, and for uniform contact at the ends of the sample.

One experiment was performed to test an etching method for producing fine points on the phosphor bronze wire intended for use as contacts in the micromanipulator. Figure 3.2 shows the circuit finally adopted, and Figure 3.3 shows one of the points produced. An etchant of one part commercial HNO_3 in three parts water was used. The variac was set for 10 volts with the switch open. Then the sample was immersed 0.5 cm in the etchant, the switch closed, and the sample withdrawn at approximately 0.5 cm/sec.

To date, no reliable data have been obtained. The potentiometer circuit is unstable, apparently because of faulty batteries. Lead-acid storage batteries have been obtained and will be used as the energy source.

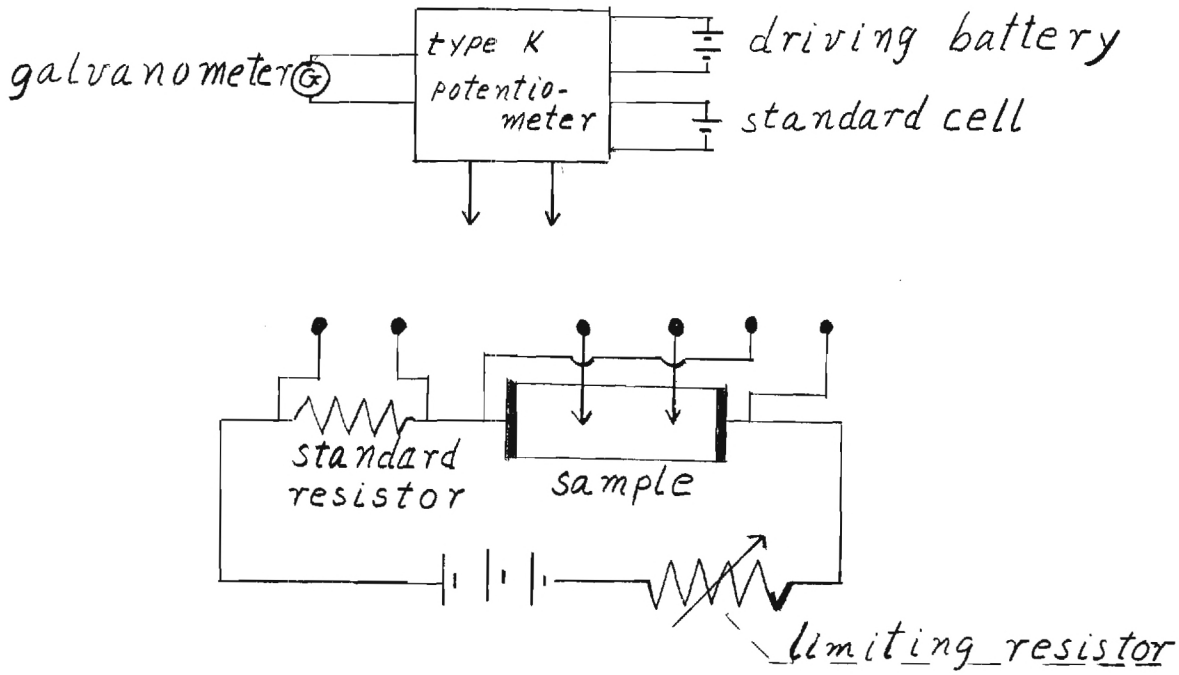

Figure 3.1 Potentiometer Circuit

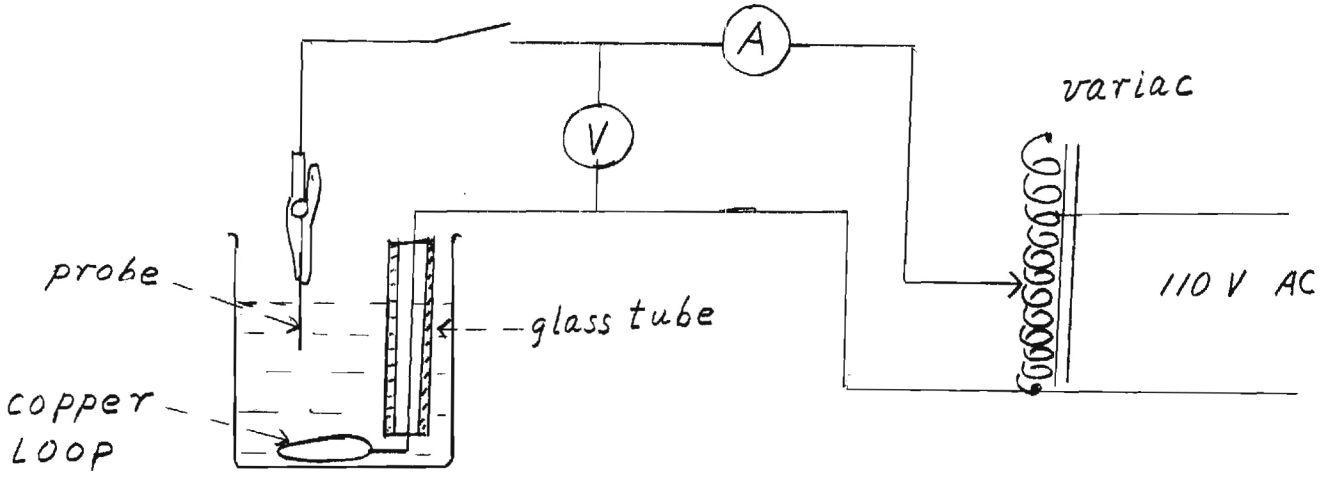

Figure 3.2 Etching Circuit

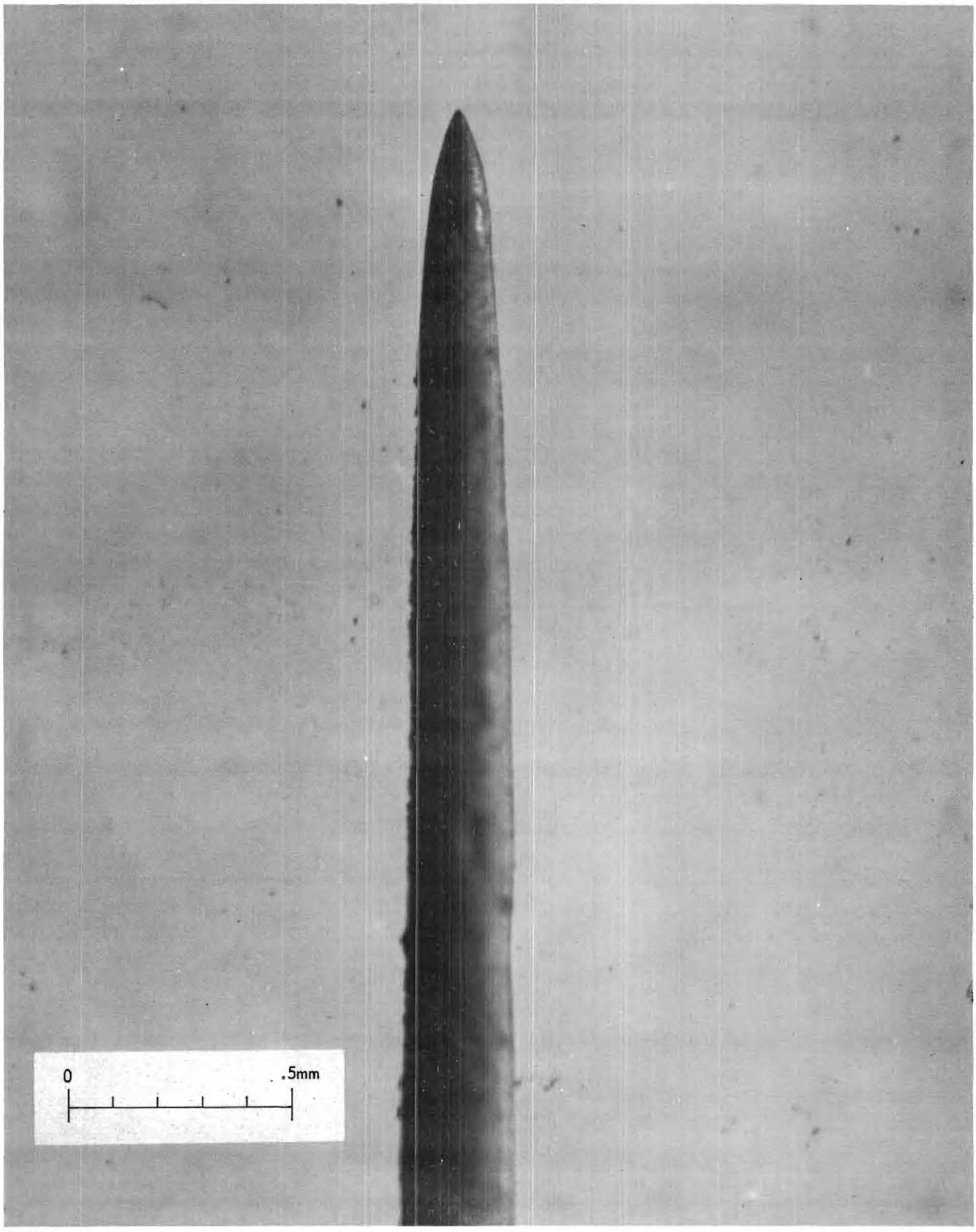

Figure 3.3 Micromanipulator Point

At the moment there are two experimental problems. The first concerns the method for measuring t, the thickness of the film. Obviously t must be known if σ and R are to be calculated. A search of the literature has disclosed several methods which are feasible. The one which appears to be the most promising is that due to Schulz[2]. It will not be described in detail here except to point out that it uses a Fabry-Perot interferometer and a sodium vapor lamp source. The separation of the D lines is used as an internal standard of length which simplifies the measuring procedures since the necessity for interpolating between fringes is obviated.

The second problem of some magnitude at the moment is the problem of procurement of a magnet suitable for the Hall effect measurements. Probably a magnetron magnet can be found which can be adapted to the needs of the moment. It may well be that the magnet used in the first experiments on single metal films will not be satisfactory to measure the effects in dual layer films if, as hoped, the latter exhibit semiconducting properties after suitable treatment.

2. Theoretical

From studies of the Hall effect and the conductivity in thin films information can be obtained concerning the type of current carrier in the material of the film, the mobility of the carriers, and their density.

Consider the conductor of Figure 3.4 which is carrying a steady current I in the X direction. A magnetic field is applied in the Z direction. This results in a transverse electric field, in the direction of the positive Y axis if the current carriers are positive charges, in the negative Y direction

if the carriers are negative charges. The resulting voltage between the two faces of the material which are perpendicular to the Y axis is called the Hall voltage.

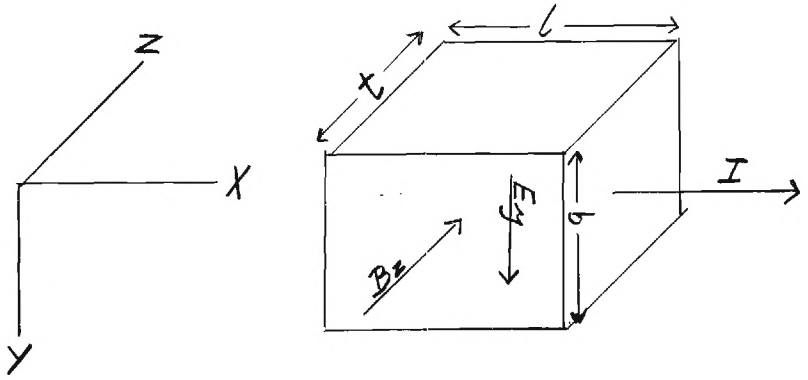

Figure 3.4 The Hall Effect

The voltage is developed because the moving charges are forced to one side by the magnetic field and accumulate on one face of the specimen until the electric field produced by these displaced charges is just large enough to counteract the effect of the magnetic field.

The total force on a moving charge is $\underline{F} = e(\underline{E} + \underline{v} \times \underline{B})$ where e is the charge, $\underline{E}$ the electric field, $\underline{v}$ the velocity, and $\underline{B}$ the magnetic field. (The M.K.S. rationalized system of units will be used in all calculations and all equations will be written so as to apply to this system directly.) Therefore,

in the steady state

$$eE_y = ev_x B_z = \frac{J_x B_z}{N} \quad ,$$

where J_x is the current density ($= Nv_x e$) and N is the number of free charges per unit volume. The ratio $E_y/J_x B_z = R$, the Hall coefficient. It will be seen from the above analysis that

$$R = 1/Ne \quad , \tag{1.1}$$

so that the Hall coefficient is the reciprocal of the free charge per unit volume.

If the Hall voltage in Figure 3.4 is V_H, then

$$E_y = V_H/b \quad .$$

Also $$J_x = I/(bt) \quad ,$$

so $$R = \frac{V_H t}{I B_z} \quad . \tag{1.2}$$

In the M.K.S. system the units of R are $\frac{\text{volt (meter)}^3}{\text{ampere weber}}$ or $\frac{\text{meter}^3}{\text{coul}}$.

The mobility, μ, of a charge is by definition its velocity in a unit field.

$$\mu = v/E$$

Therefore, $$\mu Ne = vNe/E \quad .$$

But $$vNe = J$$

so $$\mu Ne = J/E \quad .$$

But $J/E = \sigma$, the conductivity, by Ohm's Law. Therefore,

$$\mu Ne = \sigma \quad . \tag{1.3}$$

From equations (1.1) and (1.3) it may be seen that a measure of the Hall coefficient and the conductivity will yield the values of the mobility of the current carriers and their concentration, providing the carriers are all of the same kind. In the event that conduction is taking place because of two types of carriers, for example, by both electrons and holes in the case of a semiconductor operating in its intrinsic region, then the situation is more complicated, and a measure of the Hall coefficient and conductivity serves only to give two pieces of information connecting the four variables n, μ_n, p, and μ_p, where n and p are the concentrations of electrons and holes, and μ_n and μ_p are their mobilities.

B. Crystal Holder for Back-Reflection Camera

During the last quarter, work in the X-ray laboratory on Project E-102 has included the design and construction of a crystal holder for use with a flat-plate, back-reflection camera. This holder consists of three parts: (1) a small brass rod on which the crystal is mounted, (2) a universal goniometer head in which the rod is mounted, and (3) a stand for the goniometer head. Parts (1) and (3), Figure 3.5, were made in the station shop.

The advantages of this holder are:

1. The face of the specimen may be accurately positioned parallel to the film and normal to the beam by an auto-collimating device. The error in this setting is less than 30'.

2. Once the specimen to film distance has been set it is unnecessary to move either the specimen or film holder to take the picture.

3. The crystal may be rotated about each of two mutually perpendicular axes as much as $\pm 20^{\circ}$. By taking two pictures of the same crystal, differing only in the known angle between the crystal face and the X-ray beam, the orientation of the crystal can be checked. For an example of pictures of this type see Figure 3.6 in which the sample was a single crystal of germanium.

4. The crystal may be removed (on its mount) from the goniometer for polishing or etching and replaced accurately in its original position. Two advantages of the back-reflection method of crystal orientation are: (1) the accuracy improves as 2θ increases (up to $\theta = 90^{\circ}$), and (2) in most work the size of the crystal is immaterial.

Little work has been done on orientation this quarter. The next quarter's work should include the development of a rapid method for accurate orientation of single metal crystals.

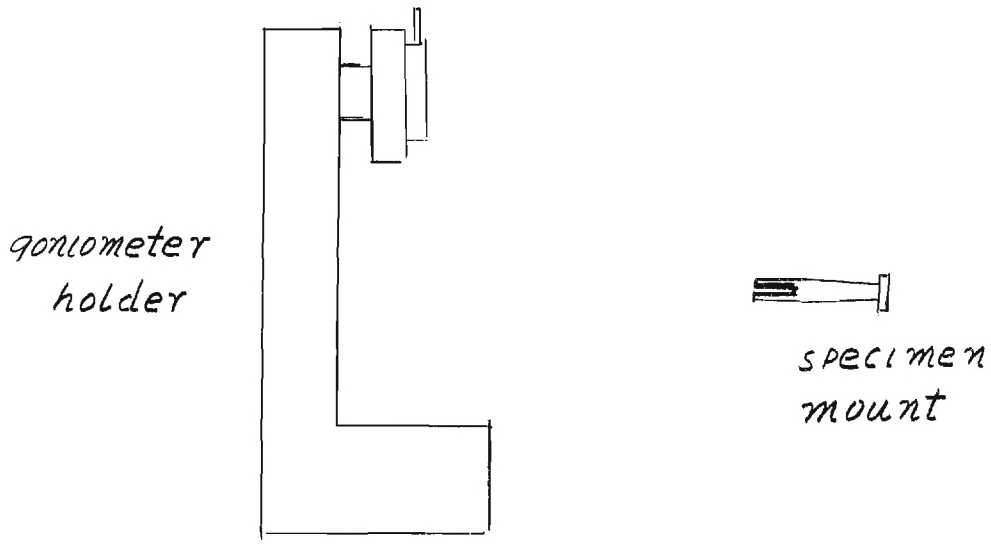

Figure 3.5 Crystal Holder

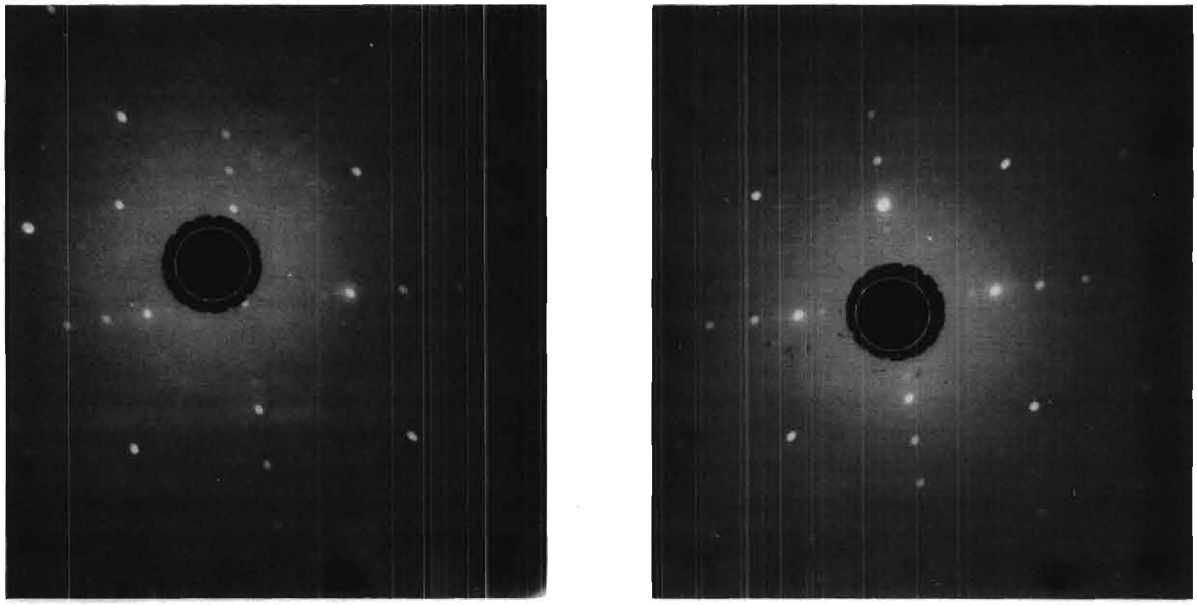

Figure 3.6 Single Germanium Crystal

IV. PROGRAM FOR NEXT INTERVAL

The work on conductivities and Hall coefficients of thin metal films will be continued. Measurements will be made both on single and dual layer films. The possibility of forming binary alloys with semiconducting properties will be studied empirically. Further X-ray work on single crystals will be carried out. A precession camera has been obtained which will give an undistorted picture of the reciprocal lattice. The potentialities of this device will be studied and it will eventually be used in a study of crystal imperfections.

V. IDENTIFICATION OF KEY TECHNICIANS

Dr. Vernon Crawford assumed directorship of Project E-102 in December, 1953, and devotes approximately one-quarter of his time to this project. Dr. Crawford is Associate Professor of Physics. He received his Doctor's degree from the University of Virginia, and he has worked on Projects 171-118 and 229-198 on the problem of frequency control.

Joseph Worth has joined the project as student assistant. He is a senior in physics.

William E. Woolf, Research Physicist, has been employed in the X-ray diffraction laboratory since November, 1952. He received his Bachelor's and Master's degrees from Emory University. He also received additional graduate training at Duke University. From 1948 to 1950 he was employed at the Argonne National Laboratory.

Ralph W. Johnson has been a student assistant in the X-ray laboratory since July, 1952. He is a senior in physics.

Approved:

James E. Boyd, Head
Physics Division

Herschel H. Cudd, Director
Engineering Experiment Station

Respectfully submitted:

Vernon Crawford
Project Director

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ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

QUARTERLY REPORT NO. 3

PROJECT NO. E-102

PHYSICS OF SOLIDS

By

VERNON CRAWFORD and R. B. BELSER

MARCH 31, 1954

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I. ABSTRACT

Work during the current quarter has covered the following fields of endeavor:

A. Resistivity and structural studies of the platinum metals ruthenium and osmium.

B. Studies of dual-layer films of gold plus aluminum before and after aging by means of electron micrography and diffraction.

C. Studies of the erosion effects of positive-ion bombardment on polished quartz surfaces.

D. Studies of the adherence of metal films to glass and quartz substrates.

II. PURPOSE

The purpose of this project is to get research in the field of solid state physics started at the Engineering Experiment Station of the Georgia Institute of Technology. Various problems in this general field will be studied for the purposes of training some investigators in the field of solid state research, of making the best use of the existing facilities, and of acquiring such additional research equipment as is needed to maintain an active solid state program. The scope of the project will undoubtedly increase as work progresses. Specific problems to be studied include:

1. Studies of the preparation of metal surfaces for examination by electron diffraction, optical microscopy, and electron microscopy of surface replicas;

2. Surface studies of single crystals;

3. The properties of single and dual layer films.

III. RESISTIVITY AND STRUCTURAL STUDIES

A. Sputtering of the Platinum Metals

Under U. S. Signal Corps Contract No. DA-36-039-sc-42453 structural and resistivity studies, before and after aging, of films of the metals palladium, platinum, rhodium, and iridium have been completed. The remaining members of this family, ruthenium and osmium, are extremely rare metals of high melting points, 2,450° C and 2,750° C respectively. No record of the previous preparation of either of these metals as thin films has been found in the literature.

A high-sputtering-rate apparatus (Figure 1) constructed from a four-inch to one-inch Dow Corning "double tough pyrex" pipe reducer and suitable electrodes allows extremely rapid sputtering of the platinum metals when electrodes of these materials are subjected to bombardment by 20 ma positive-ion currents at 3,750 volts and argon pressures near 3×10^{-2} mm of mercury. Rates range from 350 angstroms per minute for palladium down to 100 angstroms per minute for iridium. This same apparatus readily sputters ruthenium and osmium at somewhat lower rates, approximately 60 and 30 angstroms per minute respectively. The relative slowness of these latter appears to be related to oxidation effects on the cathode which retard sputtering. Although argon gas has been used as the residual atmosphere (after three separate flushings), water vapor and oxygen appear to be present to the degree necessary for partial oxidation of the metal cathode surface and of the films during deposition. A better trapping system for the sputtering apparatus is on order.

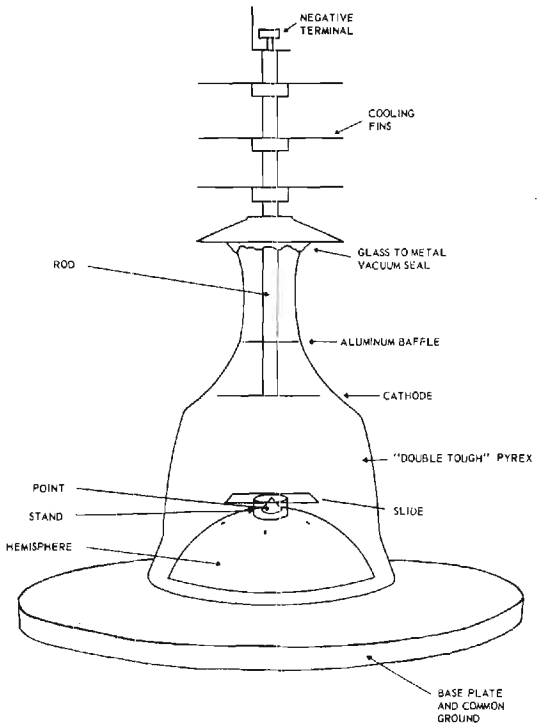


Figure 1. High-Rate Sputtering Apparatus.

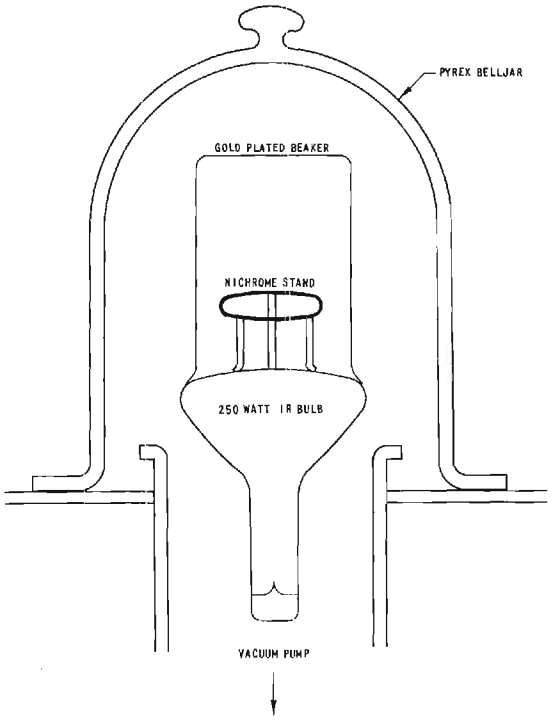


Figure 2. Infrared Vacuum Oven.

B. Resistivity Measurements

Resistivity measurements are normally made by indium soldering[1] copper leads to films on glass substrates which are approximately 25 mm x 38 mm x 2 mm in dimensions.

Resistance is measured on a Leeds and Northrup Bridge. The resistance per square is calculated from the latter measurement, corrected for the resistance of the leads.

Films of successively increased thickness were deposited on the clean glass substrates, and their resistances measured shortly after deposition. The films were then subjected to heat treatments in an infrared vacuum oven (Figure 2) at temperatures near 600° C. After cooling to room temperature, the resistances of the films were again measured. Plots of the data obtained for ruthenium and osmium are shown in Figures 3 and 4.

Calculations of the resistivity, ρ, for any film are readily made by multiplying the thickness of a film in angstroms x 10^{-8} by the resistance per square of the given film. For the ruthenium films, initial values of the ratio ρ/ρ_b were about 6.2 for 1,000 angstrom films and 1.8 after the aging treatment. For osmium these values were 17.8 and 7.7 respectively. These values are approximately four times those that might be considered normal for platinum metals.

The behavior of ruthenium is nearly typical of the other platinum metals studied, although the initial and final resistivity values are somewhat greater than those of platinum or rhodium. The behavior of osmium, on the other hand, is unique among the platinum metals and is ascribable to its ready oxidation at low temperatures (near 200° C). Behavior of this type was encountered in

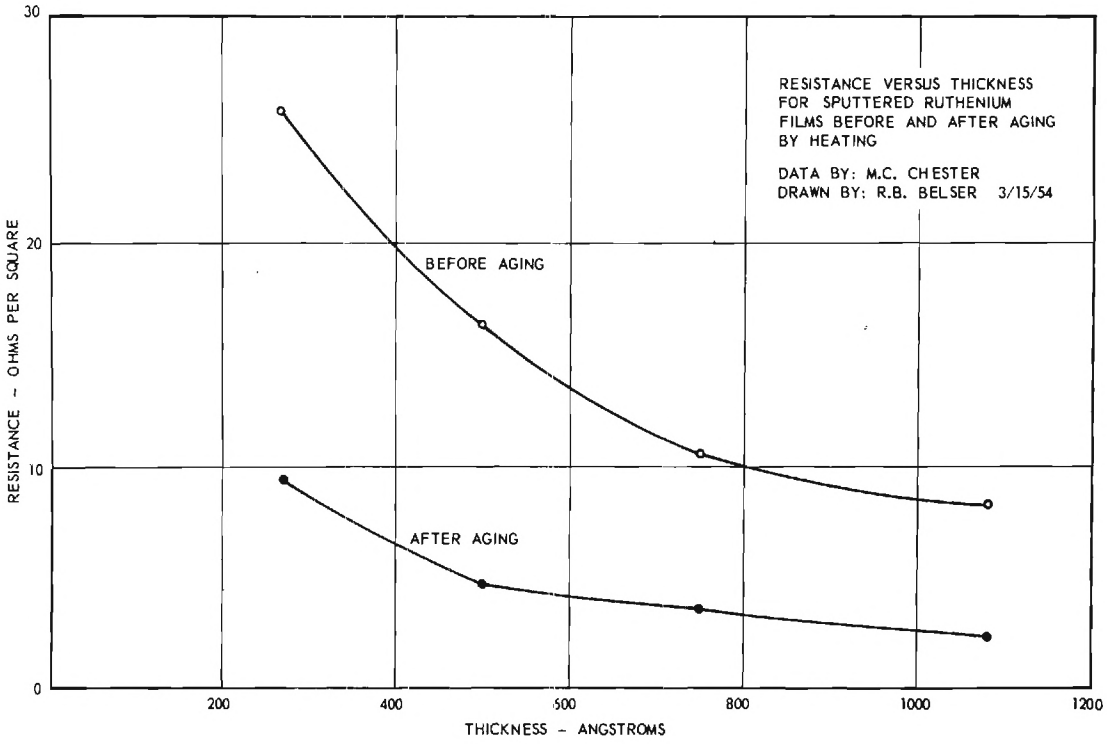


Figure 3. Resistance Vs. Thickness for Sputtered Ruthenium Films.

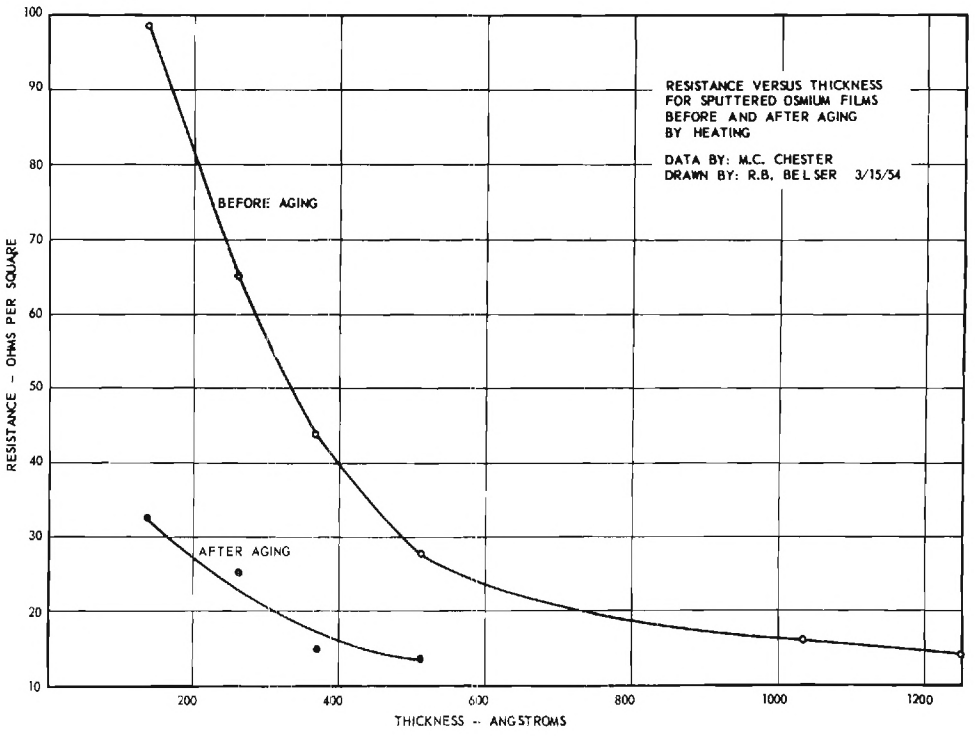


Figure 4. Resistance Vs. Thickness for Sputtered Osmium Films.

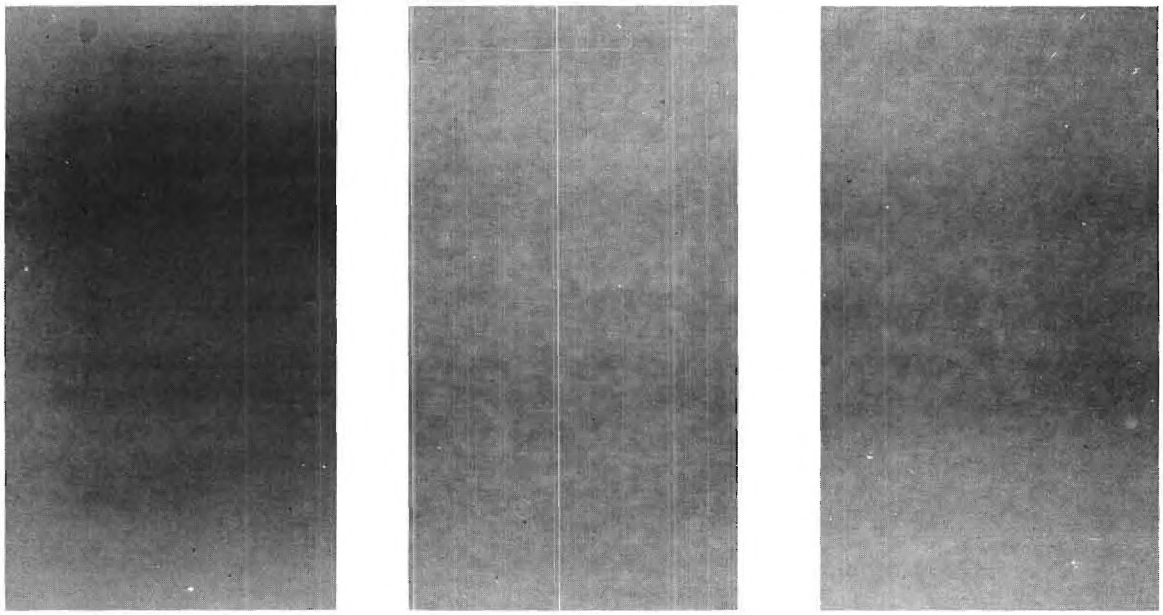
an experiment on sputtered copper which oxidizes similarly under sputtering conditions. After being heated in the infrared vacuum oven, these copper films changed from a greenish or blackish cast to the typical pink of copper next to the substrate and acquired a slight reddish cast on the top. It appears that the copper oxide in the film was largely reduced, and the resistivity was reduced to five per cent of its original value.

Both osmium and ruthenium are subject to ejection from the substrate by trapped or adsorbed gases during rapid heating, making the aging of the films which are thicker than 500 angstroms erratic and aged resistivities difficult to measure.

C. Structural Measurements

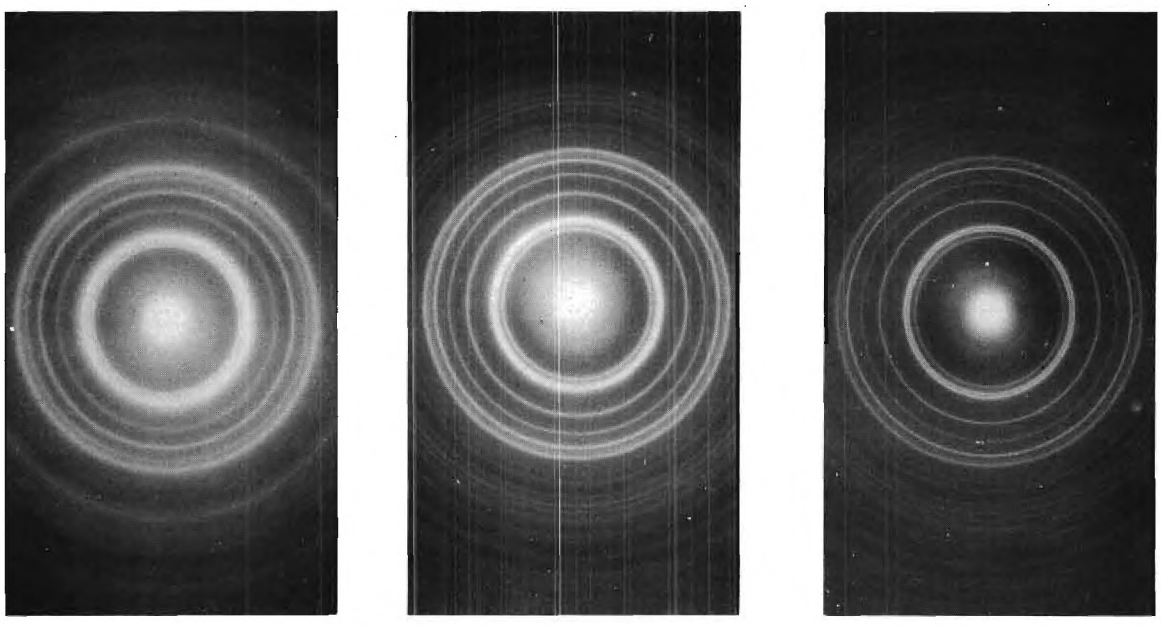
Films of ruthenium and osmium were deposited on SiO substrates for electron micrography and diffraction studies. The films, of about 100 angstroms thickness, were tested before aging and then heated successively to 400° C and 600° C in vacuum. Micrographs and diffraction patterns were made, after cooling, for each step.

The results of these tests are shown in Figures 5, 6, 7, and 8. It will be observed that the particle size in the micrographs shows only a slight coarsening with the aging treatments. Likewise the diffraction patterns show only slight changes between the initial and 400° C steps but rather marked changes in the 400° C to 600° C step. The described behavior is also typical of the other platinum metals, save palladium, and implies that a recrystallization of the film must occur in the 400° C - 600° C step. Resistance measurements also give a concurrent decrease at this temperature, and the minimum appears to be needed at approximately 600° C. This temperature has therefore



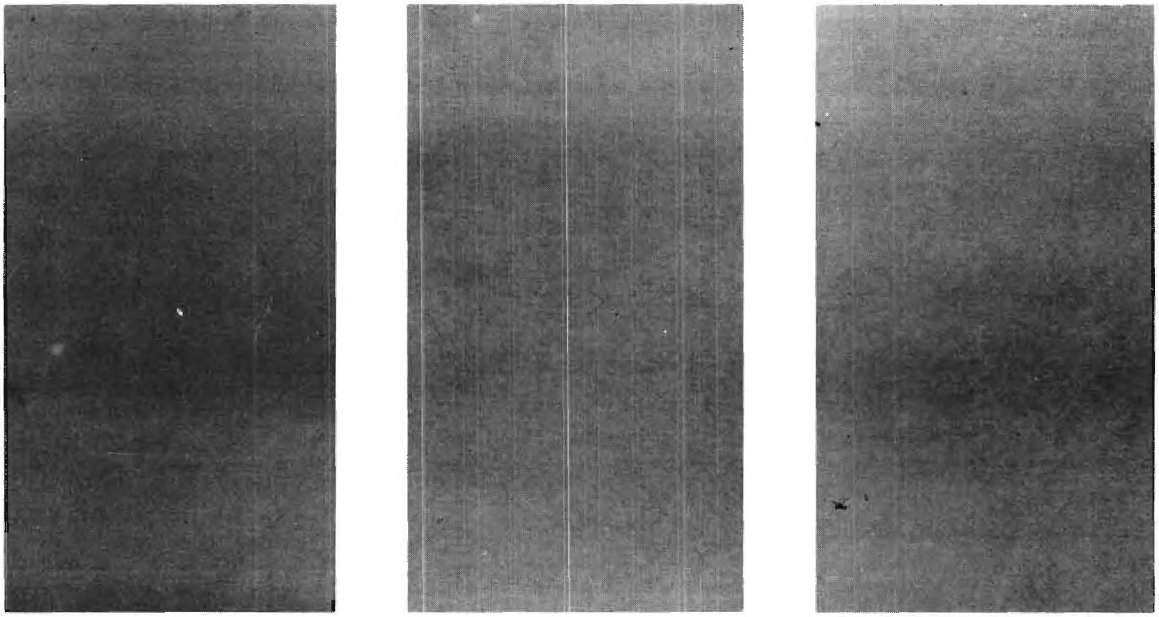
UNAGED AGED AT 400° C. AGED AT 600° C.

Figure 5. Electron Micrograph of Sputtered Ruthenium Film Before and After Aging.



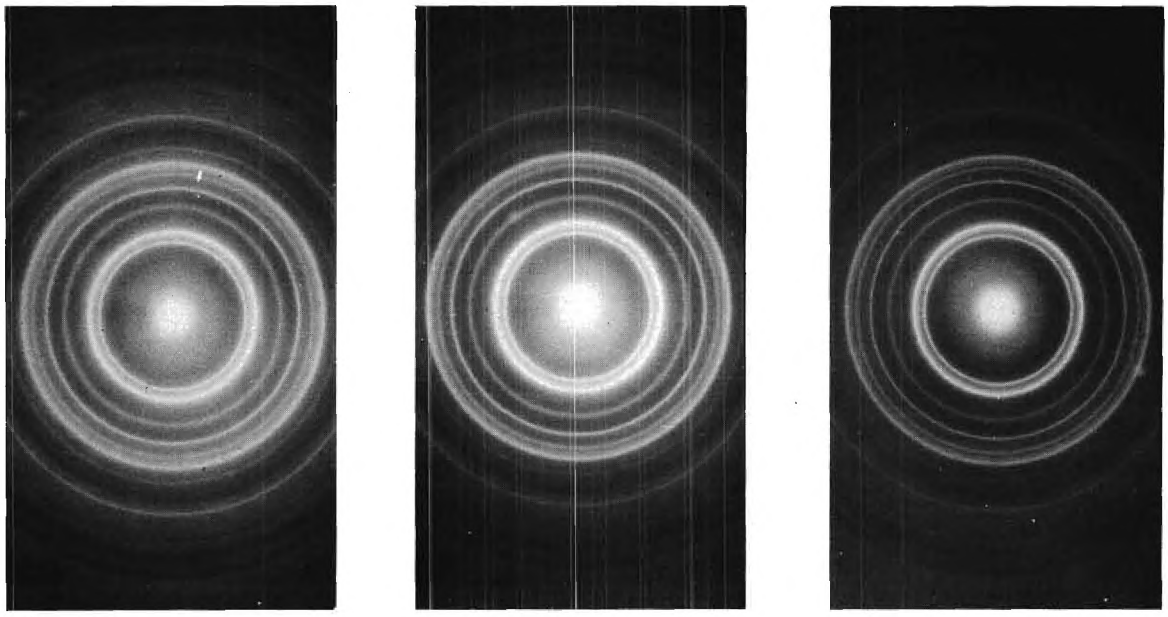
UNAGED AGED AT 400° C. AGED AT 600° C.

Figure 6. Electron Diffraction Patterns of Sputtered Ruthenium Film Before and After Aging.



UNAGED AGED AT 400° C. AGED AT 600° C.

Figure 7. Electron Micrograph of Sputtered Osmium Film Before and After Aging.



UNAGED AGED AT 400° C. AGED AT 600° C.

Figure 8. Electron Diffraction Patterns of Sputtered Osmium Before and After Aging.

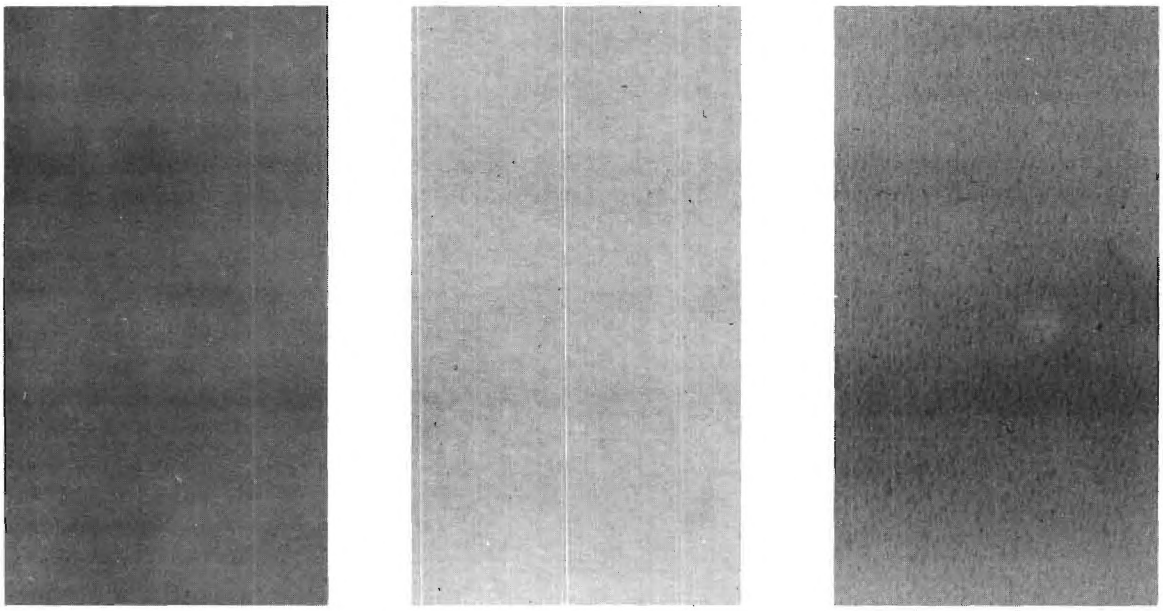
been established as an arbitrarily defined "preferred aging temperature" for these metals. Considering the high melting temperatures of these metals, and the fact that a minimum resistivity, somewhat greater than that for platinum, was found, it is possible that the preferred aging temperature may actually be somewhat above 600° C for both of these metals. To fix these values definitely, however, would require considerable care and refinement because of the previously described oxidation and "blowing off" characteristics of the films.

D. Oxidation Studies

Information in the literature states that osmium forms volatile oxides at low temperatures. Thin films of osmium and ruthenium, formed as stated in the previous section, were studied with the electron microscope and diffraction techniques, after being heated in air successively to 200° C, 400° C, and 600° C. Results obtained for osmium are shown in Figures 9 and 10. A repeat on the osmium run showed that the oxidation occurred near 200° C, and the oxide completely volatilized before a temperature of 600° C was reached. This may readily be observed from the diffraction patterns of Figure 10. For ruthenium some oxidation was noted at 600° C but obvious volatilization was not present.

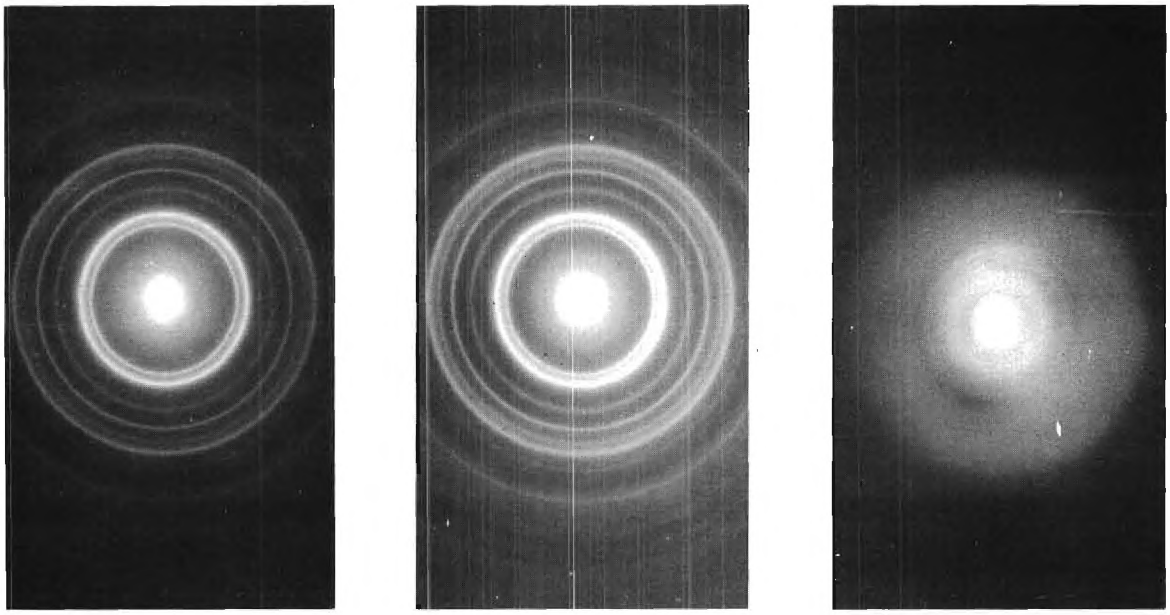
E. Miscellaneous Observations

Films of thin metals are extremely hard and adherent and are readily solderable with indium and tin-lead solders, with or without fluxes. Their uses for glass-to-metal seals, resistors, and bases for the electroplating of thicker films of other metals appear feasible. Their use or coatings for



UNAGED AGED AT 400° C. AGED AT 600° C.

Figure 9. Electron Micrograph of Osmium Before and After Heating in Air.



UNAGED AGED AT 400° C. AGED AT 600° C.

Figure 10. Electron Diffraction Patterns of Osmium Before and After Heating in Air.

piezoelectric crystals has not been tested but is questionable because of oxidation and adsorption characteristics. For the same reasons, however, their use in catalysis studies appears advisable.

IV. DUAL-LAYER METAL FILMS

A. Introduction

Extensive studies of dual-layer and simultaneously evaporated bimetal films have been undertaken under contract No. DA-36-039-sc-42453. These have been performed by studies of the resistivity, metallographic, and x-ray diffraction changes occurring in such films with artificial aging treatments by heating. Visual observation of the films and frequency measurements of piezoelectric crystals coated with these films furnish additional interesting information.[2]

B. Experimental Data

An additional available technique, not previously reported, appeared to be electron microscope and diffraction studies of similar films.

An electron-microscope (RCA type EMU-1) stage mechanism was modified so that a diffraction sample could be moved perpendicularly to the electron beam (Figure 11). A typical electron microscope SiO-coated grid was then coated by suitable masking so that on one half of the grid was a single metal film of gold and on the second half a gold plus aluminum film. Each film was estimated to be about 100 angstroms thick (from the geometry of the evaporation chamber and the amount of metal evaporated). It was now possible to make both micrographs and diffraction patterns of the sample as the sample was traversed through the beam. Results of these experiments on the initial run are shown in Figures 12 and 13. The sample was heated in a vacuum to successive temperatures of 200° C and 600° C, and suitable micrographs and diffraction

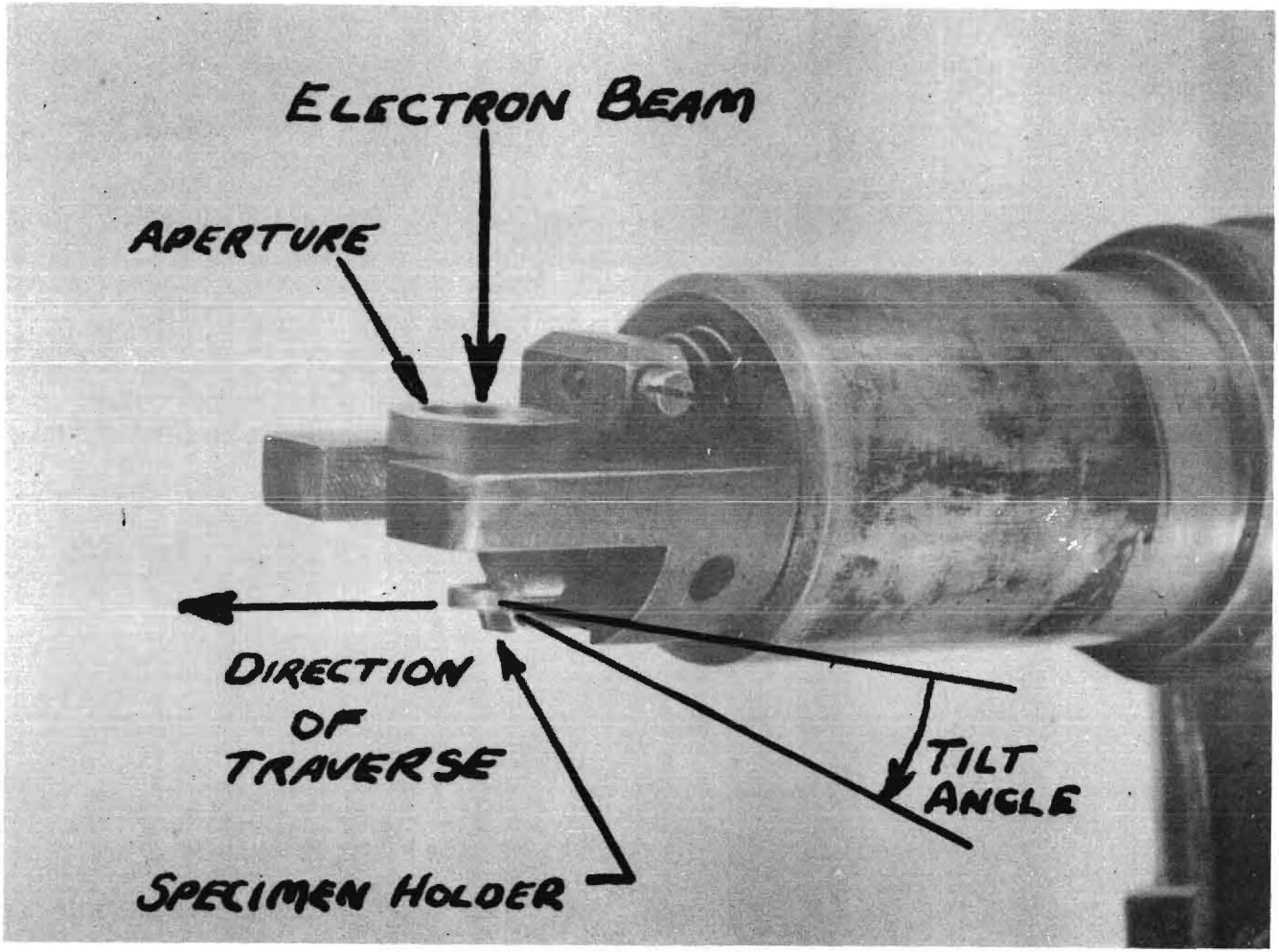


Figure 11. Modified Electron Microscope Stage Apparatus.

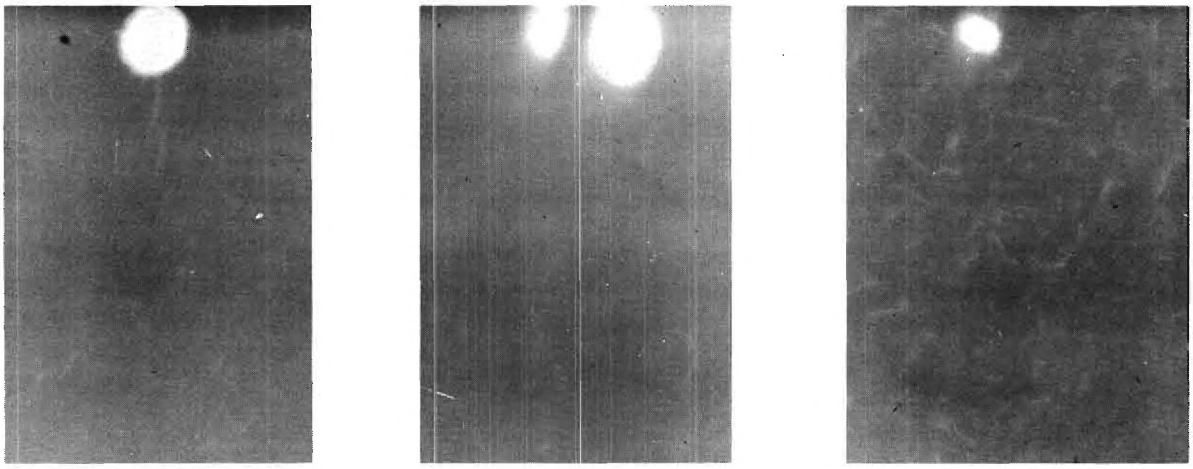


Figure 12. Electron Micrographs of Au and Al Film Taken at Three Positions of Traverse.

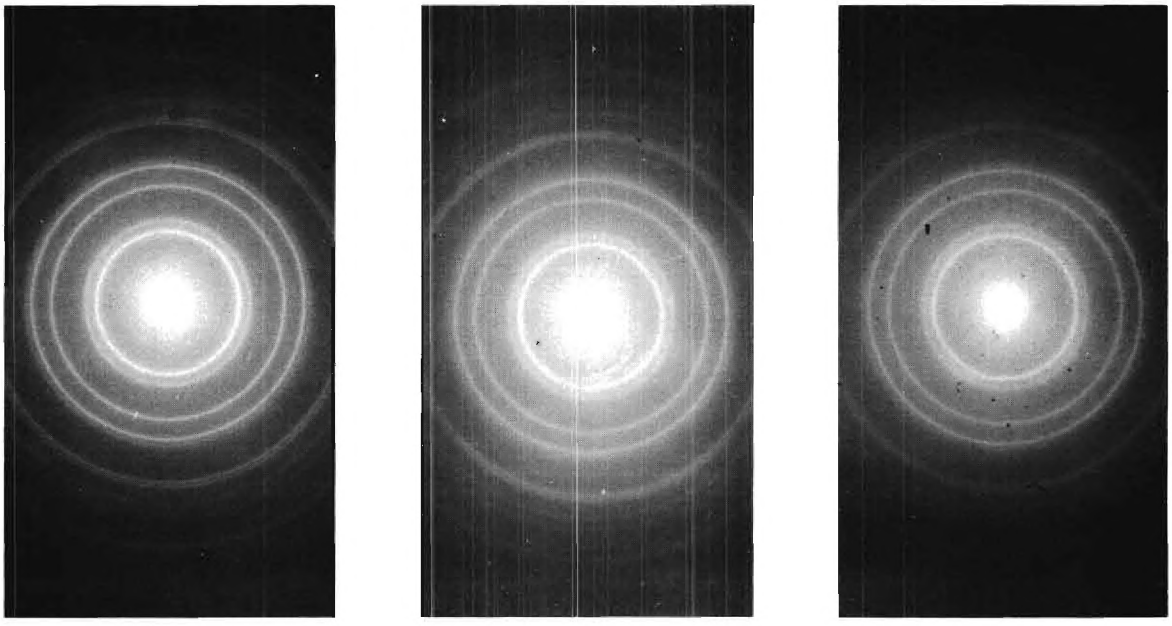


Figure 13. Electron Diffraction Patterns of Au and Al Film Taken at Three Positions of Traverse.

patterns were made. The results obtained are shown in Figures 14, 15, 16 and 17.

Although the micrographs did not give any information that was readily interpretable (except for certain aggregational effects), the diffraction patterns showed the definite occurrence of alloying of the gold plus aluminum film at a temperature of 200° C. The identified phase here was the $\beta'Au_4Al$. On heating to 600° C a considerable change in the pattern occurred but the phase was unidentifiable. It appeared to give a pattern related to a hexagonal close-packed structure, possibly Au_3Al.

A second sample was then prepared and completely coated with gold plus aluminum. The experiment was repeated with this sample. At 200° C the $\beta'Au_4Al$ phase again appeared but at 600° C still another unidentified phase was observed. Table I gives a summary of d values observed as compared with gold and aluminum separately.

C. Discussion

The gold-aluminum phase diagram is known only in part. Five intermetallic phases have been mentioned in the literature but x-ray data are available on only two. The phases observed after aging the samples at 600° C may each be phases for which x-ray data are not available.

A method of approach to an analysis of these data appears to be to repeat the experiment a number of times to observe the ability to repeat the formation of any one of the unknown phases observed. If there are only five such phases, about ten experiments should give a reasonable knowledge of the occurrence or recurrence of any given pattern. If this can be achieved and

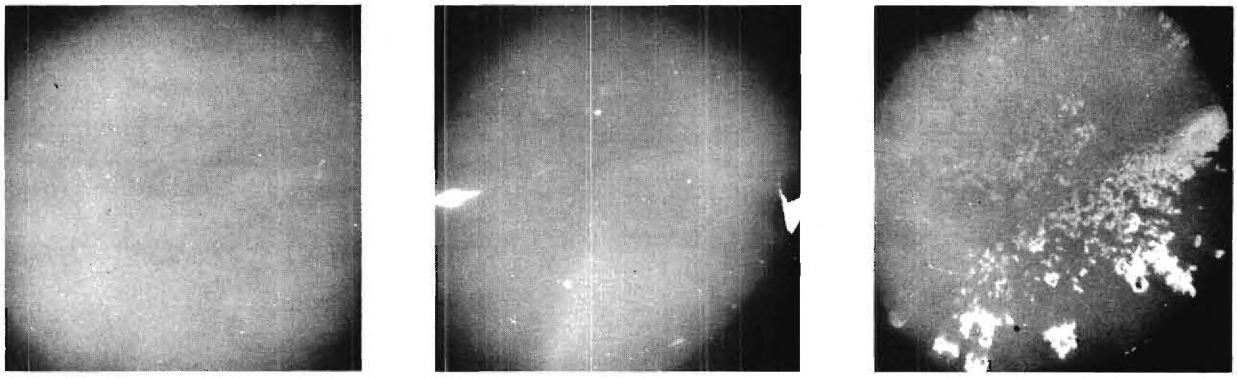


Figure 14. Low Power Electron Micrograph Showing Changes with Heating.

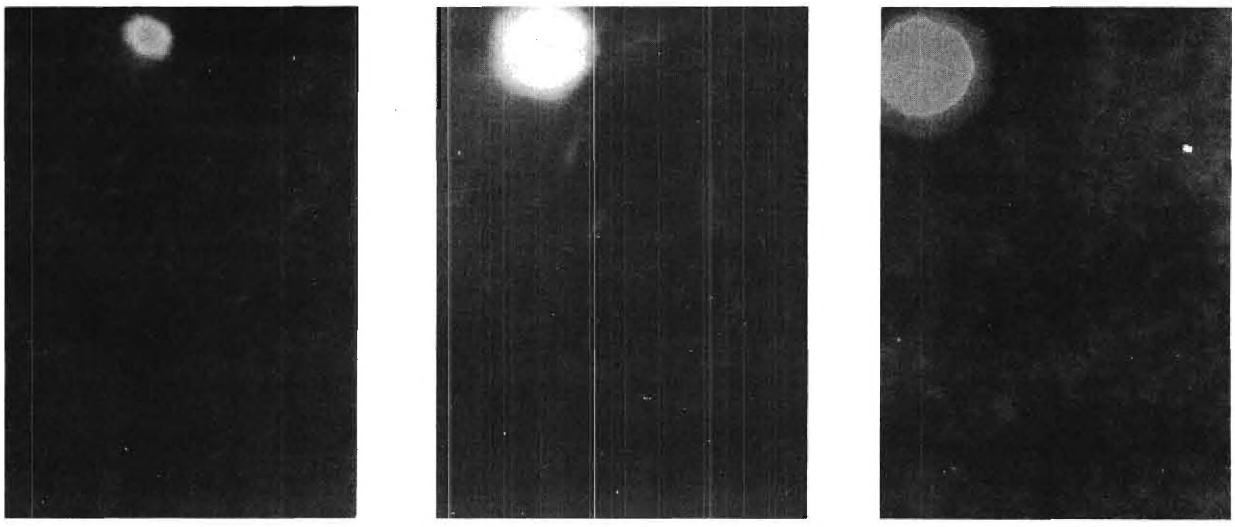


Figure 15. High Power Electron Micrograph Showing Changes with Heating.

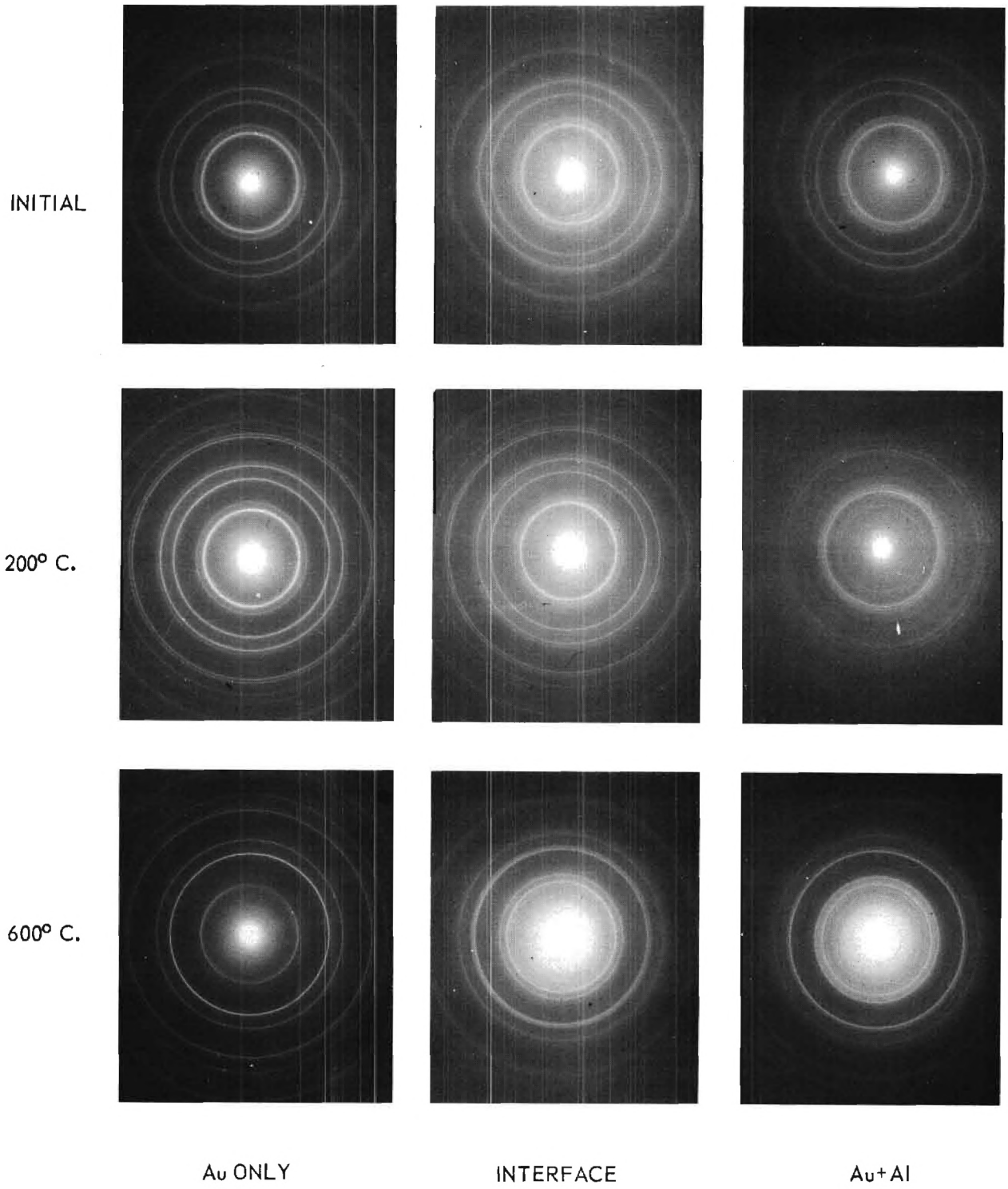


Figure 16. Comparison of Diffraction Patterns of Au and Al Films.

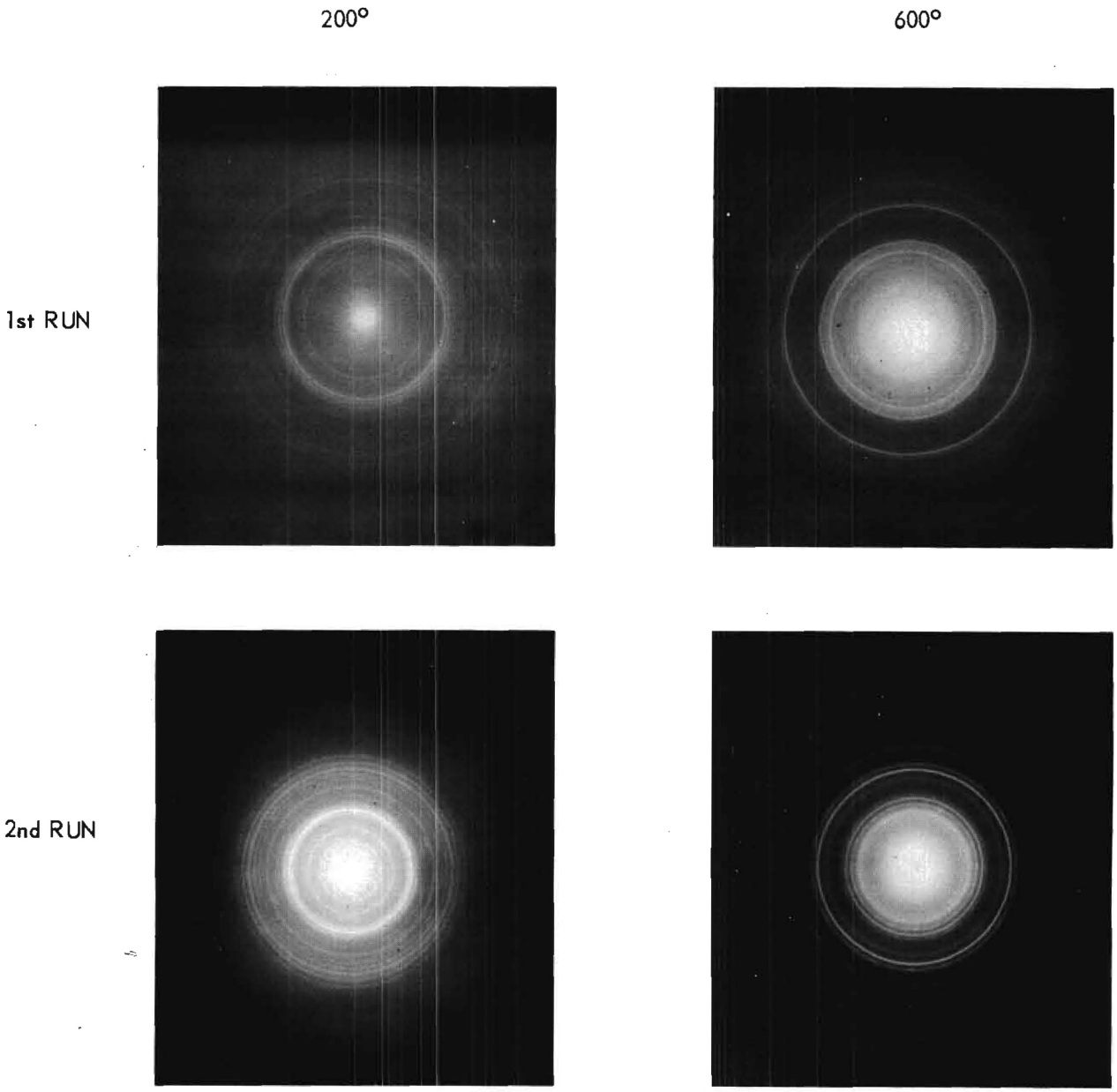


Figure 17. Recheck Comparison of Au and Al Films.

TABLE I

"D" VALUES FOR Au AND Al ALLOYS

A. d-values in angstroms for gold, aluminum, and two forms of gold-aluminum alloys, from the literature

Au	Al	$\beta'(Au_4Al)$	$\eta(AuAl_2)$
2.35	2.33	4.88	3.46
2.03	2.02	3.95	3.00
1.439	1.430	3.45	2.10
1.227	1.219	2.82	1.81
1.173	1.168	2.44	1.73
1.019		2.30	1.50
.935		2.18	1.38
.91		2.08	1.34
		1.99	1.23
			1.20

B. Measured d-values in angstroms from plates of Figures 16 and 17. Suffixes A and B on plate numbers indicate frames taken in sample regions where Au>>Al, D and E indicate regions where Au and Al are approximately equal. The letter designations on the various lines give a semi-quantitative measure of intensities according to the following scheme: V - very, B - bright, M - medium, F - faint.

Plate No. 163-349 B (200° C)		163-349 D (200° C)		163-349 E (200° C)	
2.48	VF	3.10	VF	4.92	VVF
2.33	VB	2.86	VF	3.99	VVF
2.025	F	2.37	MB	3.08	MF
1.432	B	2.30*	MB	2.82*	F
1.221	MB	2.18*	MF	2.30*	B
1.172	VF	2.10	F	2.18*	MF
.932	MB	1.45	B	2.08*	F
.907	MF	1.363	F	1.83	VF
		1.285	F	1.34	F
		1.23	B	1.28	VF

* Indicates lines matching those of Au_4Al. No reliable match with $AuAl_2$ was found.

TABLE I (continued)

Plate No. 163-351 A (600° C)		163-351 B (600° C)		163-351 E (600° C)	
2.37	MB	2.33	MB	2.81	VVF
1.45	B	2.26	F	2.40	VF
1.23	MB	2.00	VVF	2.23	B
.97	MB	1.44	B	2.15	VVF
.91	F	1.42	VB	2.08	VVF
		1.37	VVF	1.98	B
		1.233	VF	1.4	B
		1.220	F	1.35	F
		1.21	F		
		.94	MF		
		.93	F		
		.92	F		

Plate No. 163-365 D (200° C)		163-366 D (600° C)	
6.25	VVF	2.50	VVF
4.56	VF	2.36	VF
4.33	MF	2.13	MB
3.45	VVF	1.96	B
3.15	MB	1.85	VF
2.94	VVF	1.50	VVF
2.75	VF	1.325	VB
2.30*	MB	1.30	F
2.18*	B		
2.11	VF		
2.02	F		
1.96	F		

* Indicates lines matching those of Au_4Al. No reliable match with $AuAl_2$ was found.

Plate No. 163-347 A (initial)		163-349 A (200° C)		163-351 A (600° C)	
2.35	VB	2.48≠	VF	2.49≠	VVF
2.04	F	2.35	VB	2.35	MB
1.43	MB	2.04	VF	1.445	B
1.215	B	1.435	B	1.23	MB
.921	MF	1.22	B	.935	MB
.9	MF	1.17	VF	.91	F
		.926	F		
		.905	F		

≠ Indicates lines <u>not</u> corresponding to accepted values for Au.

the structure of the phases actually determined from observed d values and intensities, the technique described will allow a rather rapid survey of a number of the presently unknown binary alloying actions. Of the approximately 2,700 possible phase diagrams of binary alloys only about 600 are known and on many of these data are not at all complete.

V. EROSION EFFECTS OF THE POSITIVE-ION BOMBARDMENT OF QUARTZ SURFACES

A. Introduction

The improved adherence obtained for metal films deposited on substrates previously subjected to positive-ion bombardments is well-known. The reason for this improvement is less well established. A number of reasons for such improvement may exist. Two primary possible reasons appear to be: (1) removal of adsorbed gases from the surface of the substrate and (2) erosion of the surface such that a metal film may have improved footing. This footing consists of interstices and a greater area of contact with the substrate as compared to the area of the film exposed to removal forces by adhesives, solder, Scotch tape, and similar agencies.

B. Erosion by Ion Bombardment

It has previously been established in metal-film studies (Contract No. DA-36-039-sc-42453) that the adherence of metal films to polished quartz or glass surfaces is greatly improved by bombardment of these surfaces in the sputtering chamber for five minutes at 100 ma and 3,000 volts with the apparatus of Figure 18. To study the effect on erosion of a smooth surface by this treatment a polished quartz one-mc crystal blank was bombarded for nine successive intervals of five minutes each. A negative replica of the surface was made for the initial sample and after each five-minute interval of bombardment. The preparation of the replica and chromium shadowing were done by Mr. J. L. Brown of the electron-microscope laboratory using well-known techniques.

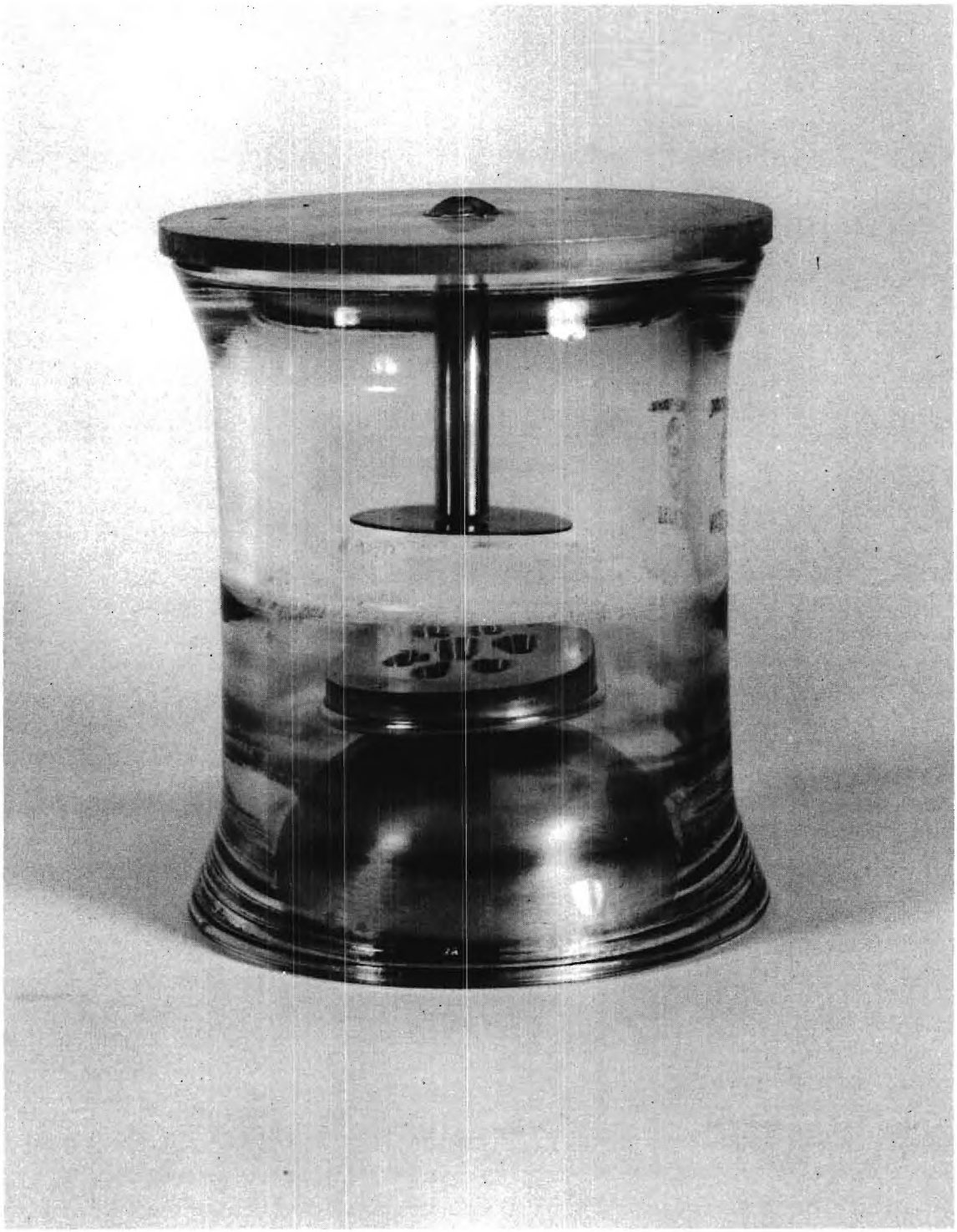


Figure 18. Positive-Ion Bombardment Apparatus.

In Figure 19 are shown the micrographs of the replicas for the initial five minute, fifteen minute, twenty minute, twenty-five minute, and forty-five minute interval. A gradual roughening in appearance was observed until about twenty-five minutes after which all marks ascribable to previous mechanical abrasion seem to have disappeared. The twenty-five minute and forty-five minute samples do not appear greatly different in roughness. During the course of the experiment, striations were observed in a number of photographs similar to Figure 20. These are presumably due to the etching away of the crystal surface along edges or planes of weakness.

C. Weight Tests and Conclusions

A similar crystal, weighed before and immediately after a thirty minute bombardment, showed a change in weight of only 100 micrograms, the balance sensitivity being 50 micrograms. After a short time, its weight returned to its original value. The inference, without repetition of the experiment, is that the loss of mass of the crystal was insignificant, whereas its loss of adsorbed gases may have been in the vicinity of 100 micrograms.

The replicas, on the other hand, did show significant erosion, and it is probable that erosion aids in adherence when bombardment is carried on for times greater than 10-15 minutes. For samples bombarded only five minutes, however, the erosion may be significantly less effective in improving adherence than is the removal of adsorbed gases prior to reversal of the current and deposition of a metal film by sputtering. A further explanation of adhesion mechanisms will be found in the next section.

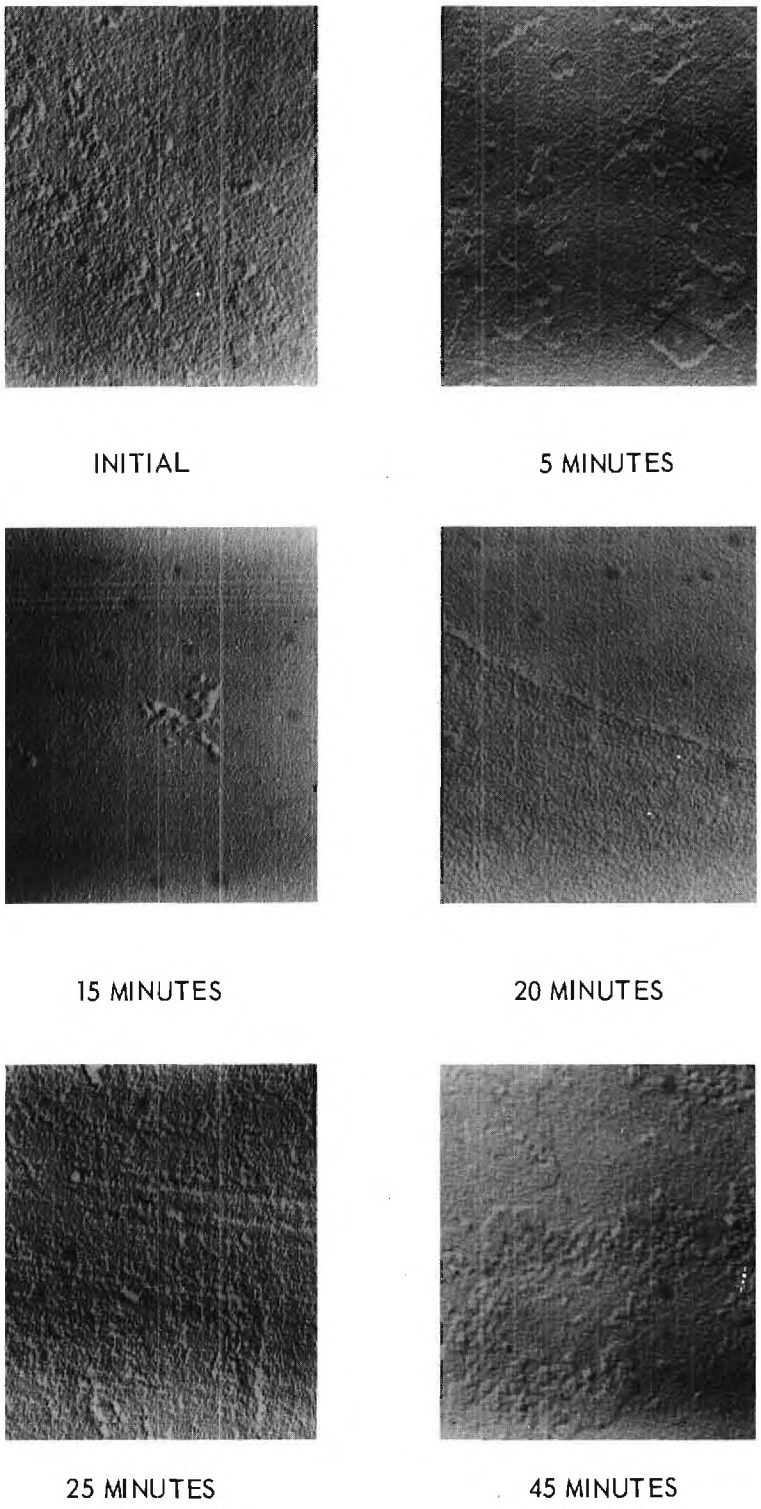


Figure 19. Replica of Initially Polished Quartz Surface After Ion Bombardment.

VI. ADHERENCE OF METAL FILMS TO GLASS AND QUARTZ SUBSTRATES

A. Introduction

As pointed out in the previous section, the mechanism of adhesion between unlike substances such as metal films and glass or quartz substrates is not well-known. It is not unlikely, however, that this bonding may consist of several mechanisms depending on the chemical activity of the metal in relation to the glass or quartz and its components and on Van der Waal forces between the metal and the substrate.

One common test for the adherence of metal films to a glass substrate is to place a piece of Scotch tape over the film and rub it securely onto the surface. The tape is then peeled from the surface and the per cent removal of the film area in contact with the tape gives a coarse qualitative test of adherence. This is in essence a "go and no go" test in which the film is usually destroyed; furthermore, results are not readily duplicable.

A second method of test that might be considered is the soldering of a metal "headed pin" onto the surface, the pin then being pulled perpendicularly away from the surface by a suitable tension device. Unfortunately solder metals frequently dissolve or penetrate the metal film, sometimes reducing the tensile strength to zero, and in general invalidating the test. Thus, a metal such as indium may penetrate the film and solder directly to the substrate. Any measurement made would then represent the adherence of indium to the substrate.

A third usable method is the attachment of a similar headed device to the film by means of a suitable non metallic adhesive. The latter method was

found to be satisfactory and is described in the next section.

B. Apparatus

A number of small aluminum cylinders were cut from a 3/8-inch diameter aluminum rod. The cylinders were properly faced in a lathe, bored with a 1/8-inch hole, and threaded for attachment to an aluminum rod. A second group of cylinders were made with the contact face turned down to 1/4 inch. A group of brass machine screws were also faced across the slotted head to form a smooth surface.

A tensile-shear machine built for solder shear tests was adapted for this experiment by construction of a hinged maple block to hold the slide and cylinder-guide rod. This apparatus is shown in Figure 21.

Several adhesives were first tested in order to find a suitable adhesive. Duco cement, Pliobond, Glyptal, and sodium silicate were used. Several brass screws were also soldered to the glass with indium. The results of these tests were shown as follows.

Adhesive	Bond Strength (lbs. per. sq. in.)
Duco	325
Pliobond	175
Glyptal	310
Sodium Silicate	Negligible
Indium Solder	300-682

The Duco proved most satisfactory and was selected for the experiment.

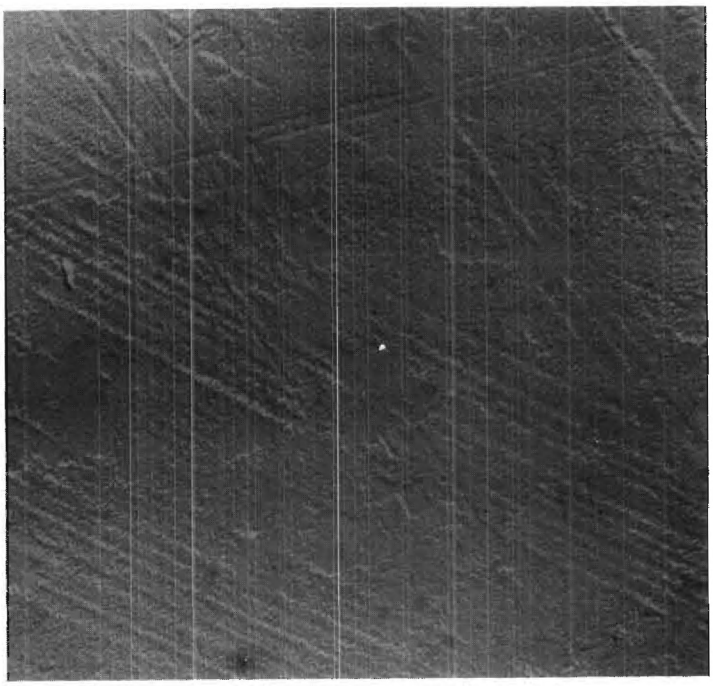


Figure 20. Replica of Quartz Surface After 20-Minute Bombardment Showing Striations.

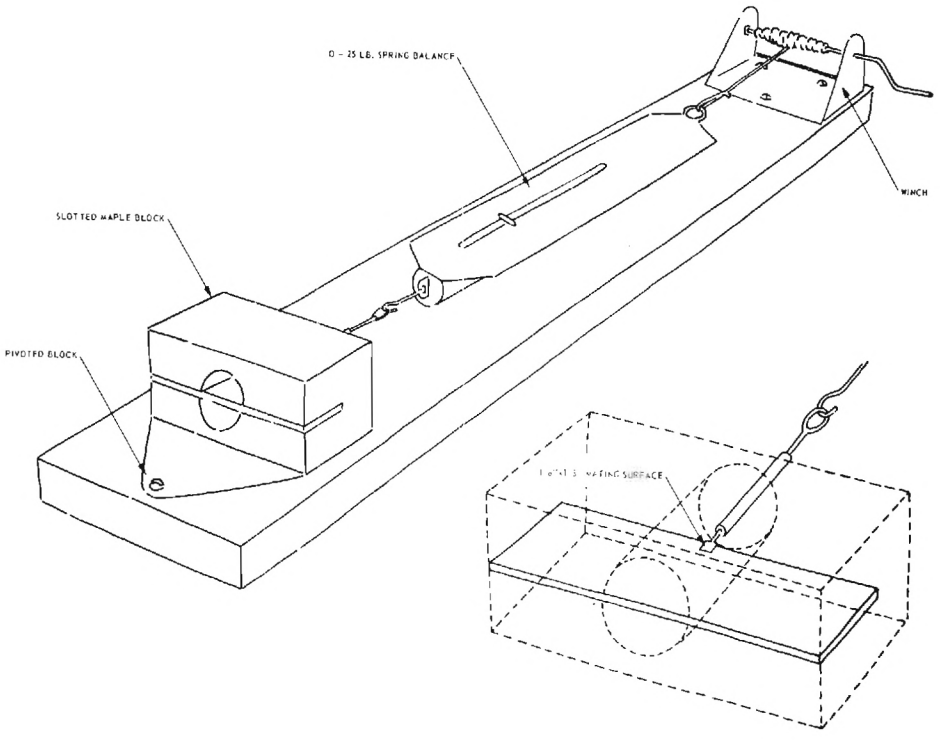


Figure 21. Solder-Shear Test Unit.

C. Adherence Experiments

1. Introduction

Certain variations in adherence between various metals to glass and the same metals deposited by different techniques or under different conditions are readily qualitatively observed. For instance it is well-known that evaporated gold adheres less well to glass than does a film of aluminum or titanium. Likewise it may readily be shown that gold deposited by sputtering is more adherent than gold deposited by normal evaporation procedures. Such films can readily be qualitatively examined by a simple scratch test with the fingernail.

2. Experimental Work

Glass substrates, cleaned by normally accepted methods including flaming before insertion in the vacuum chamber, were coated by evaporation of various metals. Aluminum cylinders glued to the film surfaces were pulled vertically from the surface with the tensile apparatus previously described.

Glass substrates were similarly prepared and coated with the same metals while the glass was held at a temperature of 250°-300° C under infrared radiation. Similarly glued cylinders were sheared with the tensile apparatus.

Additional tests were performed for metal films deposited by sputtering only and by sputtering after previous ionic bombardment for five minutes at 60-80 ma and 3,000 volts.

Data obtained for the various experiments are shown in Table II. In general, each entry represents the average of a number of values. Tests which were obviously faulty were discarded from the average. For shear tests of this nature, the higher tests are representative of the real adherence of the metal for the substrate.

TABLE II

ADHESION OF THIN METAL FILMS TO GLASS SUBSTRATES

METAL	NEP VOLTS	EVAPORATED R.T. GLASS (lbs. per sq. in.)			EVAPORATED HOT GLASS (lbs. per sq. in.)			SPUTTERED (lbs. per sq. in.)			SPUTTERED ION-BOMBARDED (lbs. per sq. in.)		
Magnesium	−2.38	169	204	260									
Titanium	−1.75	173	264	320									
Aluminum	−1.67	134	160	180									
Iron	−0.44	138	160	220									
Nickel	−0.28	148	170	220									
Lead	−0.126	97	130					218	229	320			
Copper	+0.344	91	132	175	166	194	290						
Silver	+0.97	111	166	240	212	276	320	323	362	520	250	320	320
Palladium	+0.85	108	131	150	129	164	200	170	245	300	258	258	320
Rhodium								276	338	400			
Platinum	+1.2							176	223	320	260	260	320
Gold	+1.68	94	118	150	139	164	190	163	190	240	211	272	320

NOTE: THREE ENTRIES PER COLUMN REPRESENT THE FOLLOWING: THE GENERAL AVERAGE; AVERAGE OF HIGH VALUES; MAXIMUM TEST.

	DUCO CEMENT	PLIOBOND	GLYPTAL	INDIUM SOLDER
Plain Glass	320	175	310	682

Similar data for a few metals deposited on polished quartz surfaces have been obtained and are shown in Table III.

In addition, certain tests have been made by soldering headed screws to metal films of the platinum group and to nickel films electroplated onto very thin platinum metal films deposited on glass. Adherence values were very high (800-1,000 lbs. per. sq. in.) and usually resulted in the breaking of the glass substrate before the shearing of the bond. For these metals the solder does not penetrate or dissolve the metal film and the tests appear to be valid.

D. Discussion

It is well-known that even meticulously cleaned glass or quartz surfaces are coated with adsorbed-gas layers which form in a few seconds on a cool surface exposed to atmospheric pressure. Likewise such layers appear to form readily even at pressures as low as 10^{-5} mm of mercury. That these layers are monomolecular in the cases of gases, and perhaps thicker for water vapor, has also been surmised. Langmuir[3] has shown that vapors driven from such surfaces may be composed as follows:

Water Vapor	200 parts (by volume)
Nitrogen	2 parts
Carbon Dioxide	5 parts

He has further shown that at temperatures near 500° C soft glass itself may decompose giving off higher percentages of carbon dioxide.

It is reasonable to expect then, when a metal is evaporated onto a nominally clean glass surface, that the metal atoms may first contact on the substrate surface adsorbed gas or water molecules. Figure 22A gives a simple

TABLE III

COMPARATIVE TESTS OF THE ADHERENCE OF THIN METAL FILMS OF Au AND Ag TO POLISHED QUARTZ CRYSTAL BLANKS – DEPENDING ON METHOD OF DEPOSITION

METAL	METHOD OF DEPOSITION	ADHERENCE IN LB./SQ. IN.	EXTENT OF SHEARING OF FILM FROM CRYSTAL
Ag	Evaporation	215	Complete or nearly complete shearing
Ag	Evap. with heating of substrate to 250-300° C	320	Spotty or irregular shearing
Ag	Sputtering preceded by 5' + ion bombardment	450+ (point at which bond failed-not film adherence)	No shearing
Au	Evaporation	50	Complete Shearing
Au	Evap. with heating of substrate to 250-300°	200	Irregular shearing
Au	Sputtering preceded by 5' + ion bomb.	295	Partial Shearing

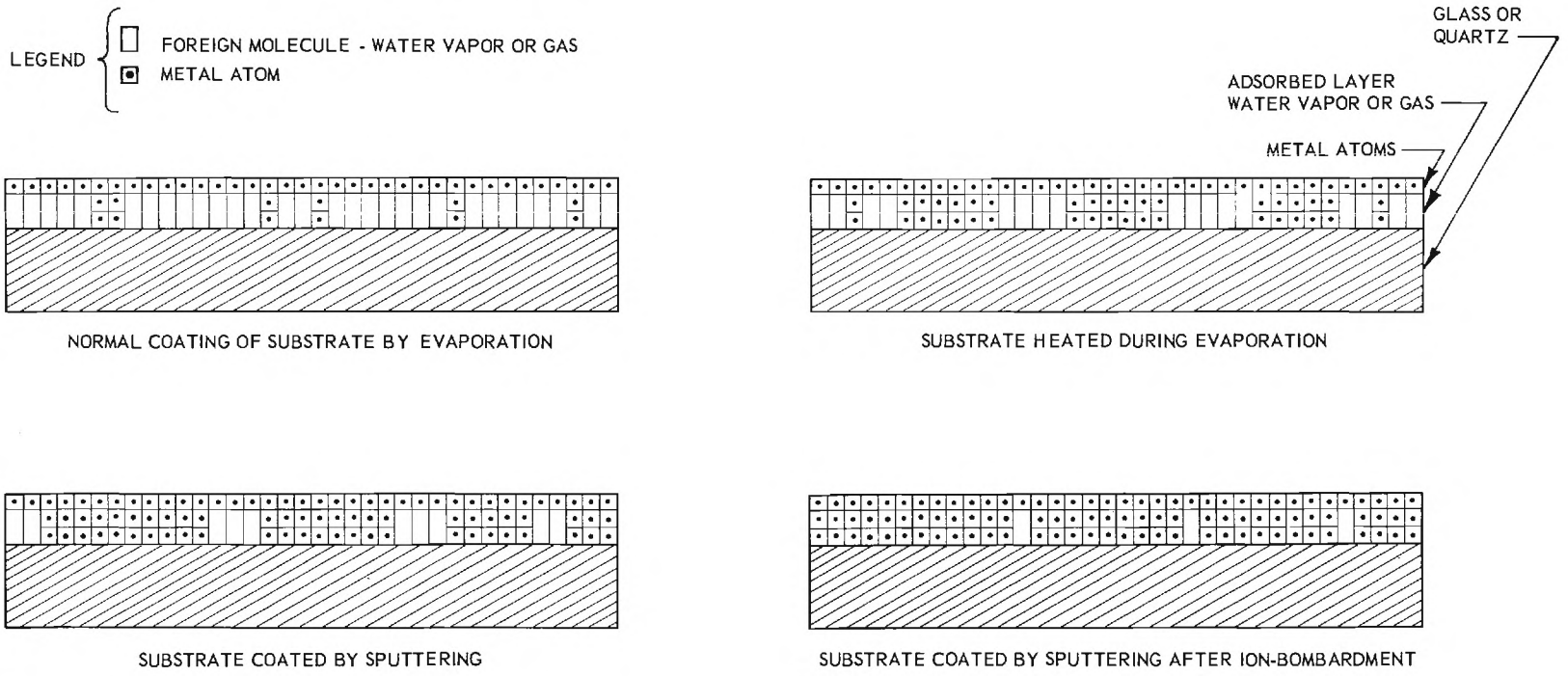


Figure 22. Sketch of One Proposed Mechanism of Adherence of Metal Films to Glass Substrates.

section of what one may expect. It will be observed that there are a few sites adjacent to the substrate filled by the metal atoms, but that the majority of the atoms must be above the gas layer. This is the picture one could reasonably expect for a noble metal such as gold. On the other hand, suppose the metal is chemically active toward the adsorbed molecules, which are really in quite concentrated form and at a relatively high temperature (as compared say with liquid air). Chemical activity between the metal atoms and the gas or water molecules would not be an unlikely occurrence in this instance. An active metal thus may attack the adsorbed-gas layer and form a larger number of sites for its own atoms, or molecules of its oxides on hydroxides, for which the metal would logically have greater affinity. This would be especially true for metals of extremely adherent oxides.

In Table II it is readily observed that there does appear to be this gradation of adherence from the active metals such as magnesium, aluminum, and titanium down to the relatively inert metals such as gold, and, in truth, that this adherence may be grossly related to the position of the metal in the electromotive series.

Upon heating the substrate, Figure 22B, sites vacated by the energized adsorbed molecules may be filled by the evaporated metal and the increased footing results in improved adhesion. This value was shown to be almost twice the first value obtained when the substrates were not heated.

For sputtered films, Figure 22C, the metal atoms are deposited during and after considerable bombardment of the substrate. Under this condition there appear to be more sites available on the substrate to be filled by the metal atoms. The formation of oxides of a number of metals during sputtering may also be effective in improving adherence.

For the substrates bombarded before sputtering, Figure 22D, optimum conditions appear obtainable such that the maximum number of sites immediately adjacent to the substrate may readily be filled. Thus, for all metals tested the adherence of these films deposited by sputtering after bombardment were so high that they approached the maximum effective limit of the glue used (300-400 lbs. per. sq. in.).

Because gold and the other metals behaved similarly in this case, it is apparent that Van der Waal forces alone are sufficient to give adherence strengths greater than 300 lbs. per. sq. in. Shear tests of all these metals, which were commonly dissolved or penetrated by soldering, were limited to the maximum shear of the glue (300-400 lbs. per. sq. in.). Many tests obviously exceeded this maximum as the films were not damaged by the tests. In no case were films which tested as much as 200 lbs. per. sq. in. removable by Scotch tape, and 150 lbs. per. sq. in. may be a more realistic value.

Now consider the solder tests to the platinum metals. The platinum metals, from all tests known, appear to be extremely well-developed even for films as thin as two to four atomic layers. Secondly, they have adsorption characteristics that are unusual. Thirdly, solders do not readily dissolve these metals. They appear to be fortuitously fitted for shear tests by solder. In addition, the known high tensile strengths of fibers or films of small dimension may be entering into these measurements. Tests on these metals may indicate that adherence values between a metal and a glass substrate may be expected to be as high as or higher than 1,000 lbs. per. sq. in. On the other hand, the other characteristics of films of these metals may be in part responsible for the high shear values obtained.

E. Conclusions

It has been shown that the adherence of a metal film for a glass on quartz substrate is dependent directly on the cleanliness of the substrate and grossly to its position in the electromotive series (or its oxide formation ability). The important part played by the adsorbed-gas layer normally present has been pointed out and the improvement in adherence which may be expected by partial or complete removal of this layer has been indicated. It is further proposed that spottiness of tests may be directly dependent on the irregularity of the removal of the adsorbed-gas layer by the mechanism of chemical combination, heating, or ionic bombardment, and that gradations from the best to the worst adherence may be dependent on the position on the film chosen for the test.

Whereas shear strengths of 300 lbs. per. sq. in. were frequently exceeded for glue joints, the weak link appeared to be glue. Shear strengths near 1,000 lbs. per. sq. in. were obtained for solder tests to nickel films electroplated onto sputtered platinum or rhodium films of only 100 angstroms thickness deposited on glass substrates. Although the mechanical strength and the perfection of thin films of these metals may be in part responsible for the high strengths shown for the adherence to glass by them, it is probable that Van der Waal forces alone may account for strengths of adherence of any metal to a glass substrate in the range 300-900 lbs. per. sq. in. It is interesting to note that the adherence of indium to glass (approximately 600 lbs. per. sq. in.) also falls within this fame range and that independent experiments conducted by a centrifugal force technique at the University of Virginia[4] gave values of

-77.5, -143, -187, -300, and -1,740 lbs. per. sq. in. for silver films deposited on hardened steel rotors. These latter values were film thickness dependent.

VII. CONCLUSIONS

Resistivity and structural studies of sputtered films of ruthenium and osmium have been presented for the first time. The similarities to the other platinum metals in structural stability with temperature are noted for the metals when they were heated in vacuum, but their subjection to oxidation, when heated in air, was readily discernible by the electron-diffraction patterns. Recrystallization temperatures near 600° C appear to exist. Osmium when heated in air forms a volatile oxide at temperatures near 200° C, and films completely volatilize at higher temperatures.

Dual-layer metal films of gold plus aluminum have been studied by a new traversing method applied to electron-micrography and diffraction techniques. The β' phase Au_4Al has been identified in diffraction patterns obtained on aging the Au + Al film at 200° C in a vacuum. Upon aging at 600° C, two new and as yet unidentified phases were observed. The technique described appears to offer considerable possibilities for future examination of unknown binary alloy systems.

The mechanism of the adherence of metal films for glass and quartz substrates has been examined first by observation of the effects of positive-ion bombardment on the erosion of polished quartz surfaces and secondly by tensile-shear tests of cylinders glued to metal films on variously cleaned or conditioned surfaces. The primary mechanism of adherence appears to be a Van der Waal action between the metal film and the substrate. This action is normally interfered with by the presence of adsorbed-gas or moisture layers. Because of the reaction between evaporated metal films and the adsorbed-gas or moisture layer, such films may have a graduated adherence to the substrate in accordance

to their electromotive-series position and oxide affinity. It is possible, in addition, that certain other chemical forces may enter into the mechanism. On the other hand, with the removal of the adsorbed layer by heating or ionic bombardment, high adherence values were obtained for all metals tested. These adherence values appeared to range from approximately 300 lbs. per. sq. in. to values near 1,000 lbs. per. sq. in. for solder tests to films of the platinum family. The 300 lbs. may represent the maximum strength of the glue used and the 1,000 lbs. may be distorted by certain peculiarities of the platinum metals and thin films in general. It may be stated, however, that Van der Waal forces alone, even for a noble metal such as gold, are able to account for adherence strengths greater than 300 lbs. per. sq. in. and that adherences of this magnitude are large enough to withstand any test of the Scotch tape nature. Secondly, adherences of this quality are sufficient for construction of commonly used devices such as plated piezoelectric crystals and mirrors.

VIII. PROGRAM FOR NEXT INTERVAL

Mr. Worth, who was doing the work on conductivities and Hall coefficients of thin metal films, has had to leave the project, at least temporarily, because of the pressure of school work. It is, therefore, somewhat doubtful when that phase will be continued.

At present it appears that work on binary alloys, using the experience gained in the thin film work, offers promise of yielding fruitful results. As a result of some work which was done last quarter, and which has not yet been reported on, it seems probable that a major effort will be devoted toward background and library research on a phenomenon of considerable interest which was turned up. Since the work in question has some security aspects, it will be described in a report with the appropriate security classification.

IX. IDENTIFICATION OF KEY TECHNICIANS

Dr. Vernon Crawford assumed directorship of Project E-102 in December, 1953, and devotes approximately one-quarter of his time to this project. Dr. Crawford is Associate Professor of Physics. He received his Doctor's degree in physics from the University of Virginia, and he has worked on Projects 171-118 and 229-198 on the problem of frequency control.

Mr. R. B. Belser is a Research Physicist with the rank of Assistant Professor. He received his M.S. degree from Emory University. His experience includes appointments as Research Assistant with the Pulp and Paper Laboratory and Research Engineer with the Southern Kraft Corporation. He has many research publications in his major field of interest, thin metal films.

Approved:

J. E. Boyd, Head
Physics Division

Paul K. Calaway, Acting Director
Engineering Experiment Station

Respectfully submitted:

Vernon Crawford
Project Director

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